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By C.yril ELLIOTT
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PREFACE

Distillation is of such importance in many industries, the scope of the subject is so great and the complementary aspects are so numerous that it is impossible in such limited space to do more than touch lightly on some of the most obvious points. In "Distillation Principles," the companion book to this, the basic physical facts and laws involved in the vaporisation of liquids were studied as an introduction to distillation on a more practical scale. The first half of the present book is likewise devoted to a consideration of fundamentals and principles which can be advantageously studied in connection with plant design. Unfortunately our knowledge of many of the factors involved in the design of distillation apparatus is fragmentary and it is only possible to draw a certain number of general but still quite definite conclusions. Yet even the few principles that can be regarded as fairly well established are frequently and flagrantly violated.

The first five chapters, which consider and analyse the processes occurring in a fractionating column, are of necessity confined to mixture of two components, since the study of complex mixtures is a matter of great difficulty and one which has consequently received very little attention. The methods of design are not therefore such as can, at present at any rate, find extensive use, but in certain cases they can be grafted on to works practice with beneficial results. The perfect column-section can be used as a criterion or standard to which an actual column can be referred. Moreover an appreciation of the processes occurring in a column and the ability approximately to estimate the effect of various changes, enable the designer to regard the plant from another angle to that of merely previous experience and purely empirical rules.

The chapter on heat transfer is a mere sketch, but

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probably sufficient to show how small is our knowledge of the subject. The remaining chapters deal in a brief manner with distillation plant in general and some applications in technical practice.

The methods of analysis and the examples in Chapters III and IV are those given by Prof. E. H. Leslie and are acknowledged in the text. They have been given in preference to the author's own analysis, which is a hybrid.

The author has coined a new expression "equilibrium" distillation and condensation, to distinguish it from "simple" distillation.

C. Elliott.

June 1925.

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DISTILLATION IN PRACTICE

CHAPTER I

SIMPLE DISTILLATION

In the companion book to this ("Distillation Principles"), the underlying principles of the vaporisation of liquids were explained, and it is assumed in the following that these fundamentals are known. Since the study of mixtures containing more than two components is complex, and at present very incomplete, the discussion in the first part of this book is confined mainly to binary mixtures.

Types of Binary Mixtures.—Possible mixtures of two liquids can be classified as

(1) Non-miscible.
(2) Partly miscible.
(3) Miscible in all proportions.

(1) *Non-Miscible.*—If a mixture of non-miscible liquids is distilled, the boiling point is lower than that of either component at the same pressure. The composition of the vapours can be calculated from the partial pressures, is constant and independent of the relative amounts of the components of the mixture provided that they are present in sufficient amount.

(2) *Partly Miscible.*—If the liquids are partly miscible, the boiling point is higher than that calculated on the assumption of non-miscibility. The vapour composition is constant so long as two layers are present, but differs from that calculated on the above assumption, the difference increasing with the mutual solubility of the components.

(3) *Miscible in all Proportions.*—These can be subdivided into three classes :—

(3*a*) Without a constant boiling point.
(3*b*) With a maximum constant boiling point.
(3*c*) With a minimum constant boiling point.

With all three classes the boiling point and vapour composition vary with and are dependent on the composition of the mixture. In classes (3*b*) and (3*c*) there is one particular composition for which the boiling point is a maximum and a minimum respectively, and at which the composition of mixture and vapour is identical. Mixtures with constant boiling points cannot be separated by distillation only.

Since the distillation of mixtures of classes (1) and (2) is comparatively simple and easily appreciated, and as classes (3*b*) and (3*c*) can be regarded as particular cases of (3*a*), the ensuing discussion is concerned mainly with the distillation of binary mixtures of miscible liquids which have no constant boiling point.

Vapour Composition.—When a mixture of two miscible liquids is distilled, the vapour is richer in the more volatile component than the residue. The relation between the composition of a mixture and that of the vapour in equilibrium with it can be represented by a curve drawn with the compositions of the mixture as abscissæ, and those of the evolved vapours as ordinates.

Boiling point–composition curves can also be drawn in which compositions of mixture and equilibrium vapour are abscissæ and temperatures are ordinates. From these can be learnt, not only the composition of the vapours in equilibrium with any given mixture, but also the boiling point of that mixture under the constant pressure for which the diagram is drawn and therefore the temperature of the evolved vapours.

Consider the boiling point–composition curve, Fig. 1. A mixture of composition C' contains AC' fractional amount of the more volatile component B and BC'

fractional amount of A, where $AC' + BC' = 1$. For convenience and to avoid confusion, the compositions of mixtures and vapours can be referred to points on the lower (liquid) or upper (vapour) curve instead of the horizontal composition axis. Thus a mixture of composition C' can also be defined as having a composition C'_{LS}, the horizontal distance between the point C'_{LS} and the vertical co-ordinate being the same as the distance AC'. The reason for using the particular notation adopted will be indicated later (p. 26).

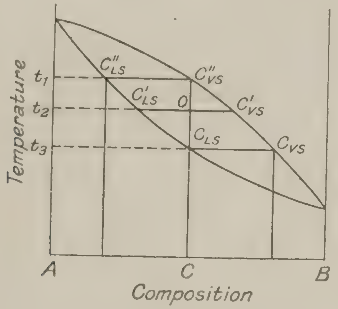


FIG. 1.—Boiling Point–Composition Curve.

Equilibrium Distillation.—If the solution is distilled under such conditions that the vapour and the mixture remain in contact and are kept in equilibrium, and if the original composition is C'_{LS}, the residue becomes progressively poorer in the more volatile component, B, its composition being given by points on the lower curve to the left of C'_{LS}. When a composition C''_{LS} is reached, the vapour has the same composition as the original mixture, *i.e.*, $C''_{VS} = C'_{LS}$. As the total amount of the liquid and vapour has supposedly not changed, at this point all the liquid must have been changed into vapour. Clearly, although the liquid has been becoming richer in the high-boiling component, the final enrichment is C''_{LS}, and the amount is infinitesimal.

Under similar conditions regarding contact and equilibrium between liquid and vapour, consider an intermediate point where the composition of the mixture is C''_{LS} and that of the vapour in equilibrium is C''_{VS}. If a mixture of weight L_S and composition C_{LS} is distilled until the residue weighs L'_S with a composition C''_{LS}, and if the vapours weigh V with a composition C'_{VS} then

$$L_S = L'_S + V$$

Considering the more volatile component B, we have

$$L_S C_{LS} = L'_S C'_{LS} + VC'_{VS}.$$

Substituting $L'_S + V$ for L_S in the second equation, we have

$$L'_S(C_{LS} - C'_{LS}) = V(C'_{VS} - C_{LS})$$

or

$$\frac{L'_S}{V} = \frac{C'_{VS} - C_{LS}}{C_{LS} - C'_{LS}} = \frac{\text{weight of residue}}{\text{weight of vapour}}$$

$$= \frac{\text{lineal distance } C'_{VS}O}{\text{lineal distance } C'_{LS}O}.$$

Similarly,

$$\frac{\text{weight of residue}}{\text{total weight}} = \frac{\text{lineal distance } C'_{VS}O}{\text{lineal distance } C'_{LS}C'_{VS}},$$

and

$$\frac{\text{weight of vapour}}{\text{total weight}} = \frac{\text{lineal distance } C''_{LS}O}{\text{lineal distance } C'_{LS}C''_{VS}}.$$

Simple Distillation.—If, however, the vapour formed during distillation is removed from contact with the liquid either continuously or at intervals, the distillate contains a greater amount of the more volatile component than the residue, and as distillation proceeds both distillate and residue become poorer in this component and richer in the less volatile constituent. By continuing the process, the composition of the residue will gradually approach that of practically pure A, but here also the yield of enriched solution is relatively very small.

By this process, however, it is possible to proceed to a practically pure constituent of the solution.

In simple distillation, therefore, the vapours as evolved are assumed to pass out of the still without any portion being liquefied except in an extraneous condenser. If the relation between the composition of mixture and vapour were as simple as it is in the case of non-miscible liquids, the course of the distillation could be easily followed, but this is, in general, far from being so. Since the object in distilling a mixture is to separate the components either partially or completely, it is necessary to know at any period in the operation how far progress has been made towards this desired end. If the operation is stopped when, say, half the original mixture is distilled over, the distillate is richer in the more volatile component B than the residue, but the actual or relative amounts are not known.

Suppose that a binary mixture contains a fractional amount C_{LS} of the more volatile component, and that it gives off vapour containing a fractional amount C_{VS} of that component. If L_S be the initial weight of the mixture, and if a differential amount dL is vaporised, the composition of the residue becomes $(C_{LS} - dC)$. Considering the more volatile component B, we have

$$\begin{aligned} C_{LS}L_S &= (C_{LS} - dC)(L_S - dL) + C_{VS}dL \\ &= C_{LS}L_S - C_{LS}dL - L_S dC + dC \,.\, dL + C_{VS}dL \end{aligned}$$

Neglecting differentials of the second order $dC \,.\, dL$

$$dL(C_{VS} - C_{LS}) = L_S \,.\, dC$$

or

$$\frac{dL}{L_S} = \frac{dC}{C_{VS} - C_{LS}}.$$

To ascertain the amount of liquid to be distilled in order to change the composition of the residue from C_{LS}, the original composition of the liquid in the still, to any other composition C''_{LS}, it is necessary to evaluate the integral equation

$$\int_{L}^{L'} \frac{dL}{L_S} = \int_{C}^{C'} \frac{dC}{(C_{VS} - C_{LS})}$$

or

$$\frac{L'_S}{L_S} = \int_{C_{LS}}^{C'_{LS}} \frac{dC}{(C_{VS} - C_{LS})}.$$

However, the relation between C'_{LS} and C_{VS} is, in general, complex and inexpressible by a simple formula. The value of the integral can be found in a very easy manner by drawing the curve giving $1/(C_{VS} - C_{LS})$ as a function of C_{LS}. Thus in Fig. 2 the values of the composition of the liquid in the still, C_{LS}, are abscissæ, and those of $1/(C_{VS} - C_{LS})$ are ordinates, the relation between C_{LS} and the composition of the vapour, C_{VS}, being obtained from the curve drawn from data experimentally obtained. Actually Fig. 2 is the curve for ethyl alcohol and water, the data being given in Table IX (p. 133). From this latter table for any value of the composition

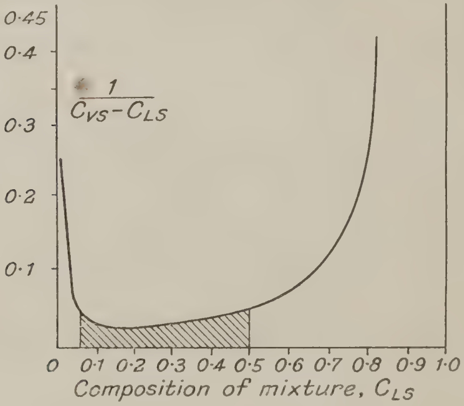


FIG. 2.—$\frac{1}{C_{VS}-C_{LS}} \sim C_{LS}$ Curve.

of the liquid in the still, C_{LS}, the corresponding value of the composition of the vapour in the still, C_{VS}, can be determined, and therefore $(C_{VS} - C_{LS})$ and $1/(C_{VS} - C_{LS})$ can be calculated. *To obtain the value of the integral it is only necessary to measure the area between the curve, the axis of the abscissæ and the ordinates at C and C'.*

For example, if a mixture of equal weights of water and ethyl alcohol is distilled until the residue contains only 5 per cent. of alcohol by weight, the composition and weight of the distillate can be readily ascertained. The area shown shaded represents the value of the integral between $C_{LS} = 0{\cdot}5$ and $0{\cdot}05$, measures $1{\cdot}075$, and is negative. We therefore have

$$\log \frac{L'_S}{L_S} = -1{\cdot}075$$

or, making L_S, the weight of the original mixture, $= 1$,

$$\log L'_S = -1{\cdot}075 \text{ or } L'_S = 0{\cdot}3413.$$

The distillate is therefore $1 - 0{\cdot}3413 = 0{\cdot}6587$. The remaining calculations are as follows :—

One grm. of original mixture contains	0·5000	grm. of alc.
Alcohol in the residue (0·3413 × 0·05)	0·0171	,,
Alcohol vaporised	0·4829	

The strength of the distillate is therefore

$$\frac{0{\cdot}4829 \times 100}{0{\cdot}6587} = 73{\cdot}3 \text{ per cent. alcohol.}$$

In the same way with any other pair of liquids, if the relation between the composition of liquid and vapour is known, the progress of the distillation can be followed for any initial and final composition of the mixture. From the data so obtained other curves could be drawn, *e.g.*, for alcohol and water a curve giving the amount that must be distilled over from any mixture in order that the residue may contain only a stipulated amount of alcohol.

Equilibrium Condensation.—Analogous to the case of equilibrium distillation already discussed, that of equilibrium condensation can be considered, the assumed conditions being as before that liquid and vapour are maintained in contact and in equilibrium. When a binary mixture of vapours of composition C''_{VS} (Fig. 1) is partly condensed, the liquid formed is richer and the vapour remaining is poorer in the less volatile component A. Under the assumed conditions and as condensation proceeds, the residual vapour becomes progressively poorer in the high-boiling constituent until finally a composition C_{VS} is reached where the liquid has the same composition C_{LS} as that of the original vapour, C''_{VS}.

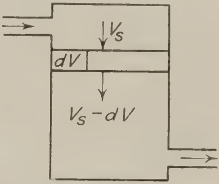


Fig. 3.—Condenser Diagram.

As the total amount of the liquid and vapour has supposedly not changed, at this point all the vapour must be changed into liquid. Clearly, although the vapour has been becoming richer in the more volatile component, the final enrichment is C_{VS} and the amount is infinitesimal. For an intermediate composition, the same relationship exists between the amount of vapour and liquid as was discussed on p. 16.

Simple Condensation.—In the same way as simple distillation, the simple condensation of a mixture of two vapours can be considered, assuming that the condensate is removed from contact with the residual vapour as fast as it is formed.

Consider a condenser shown diagrammatically in

Fig. 3, and take two horizontal sections infinitely near to each other. Across the upper section there passes the weight V_S (of vapour from a still) containing a fractional amount C_{VS} of the more volatile component. Across the lower section there passes the weight of vapour $V_S - dV$ containing $C_{VS} + dC$ of the more volatile component. In this case, the sign between C_{VS} and dC is positive, since the vapour is enriched. Finally, between the two sections a weight dV of condensate is formed containing a fractional amount C_L of the more volatile component. As the amount of this more volatile component remains unaltered, we can write

$$V_S C_{VS} = (V_S - dV)(C_{VS} - dC) + C_L \,.\, dV,$$

whence we obtain by completing the calculations as before

$$\log \frac{V'_S}{V_S} = \int_{C_{VS}}^{C'_{VS}} \frac{dC}{C_{VS} - C_L}.$$

To evaluate this integral, it is necessary to draw a similar curve to that shown in Fig. 2, but with values of C_{VS} as abscissæ, and those of $1/(C_{VS} - C_L)$ as ordinates. By measuring the area between the curve, the axis of the abscissæ and the ordinates at C'_{VS} and C_{VS}, the value of the integral can be found. The remaining calculations are then similar to those given under simple distillation.

CHAPTER II

FRACTIONATION

Fractional Distillation.—The object of distillation is to effect the separation of two or more liquids of different volatility. The word fraction implies a part of the whole, and simple distillation, as already described, is the simplest form of fractional distillation. One fraction or part is obtained, the distillate, or two fractions, if we include the residue. It is convenient to give the term fractional distillation a wide application.

From the example given in Chapter I, we see that, starting with such a rich mixture as that containing equal weights of alcohol and water and distilling off some 65 per cent. of the original weight, a distillate is obtained with 73·3 per cent. alcohol while there is still 5 per cent. alcohol in the residue. As regards separation, the result is not satisfactory. The operation could be repeated with the distillate, giving a second distillate still richer in alcohol, and by further similar operations a high-strength alcohol could be obtained, but the amount would be small, since the distillate decreases with each operation.

Some improvement as regards separation can be obtained by performing the distillation in a systematic manner. The distillate can be collected in a number of separate fractions instead of one large one, and clearly the richness of each fraction in the more volatile component would decrease progressively. The method can best be shown by referring to Fig. 4, which is for benzene and toluene, and is taken from Young ("Distillation Principles and Processes," 1922, p. 98). Starting with a mixture containing 100 grams of toluene and an equal weight of benzene, the fractions were collected between definite temperature ranges. The first distillation gave 9 fractions and a residue of pure toluene. The first fraction (9·75 grams) was redistilled until the temperature

89.2 and then up to

had risen to 89·2°[1] then the second fraction was added to the residue and the whole distilled up to 92·2°, when the third fraction was added to the residue, and so on. After four complete fractionations in this way, 42·1 grams of pure toluene and 31·55 grams of benzene boiling within 1° were obtained. An additional ten operations (not shown) resulted in the recovery of 88·8 grams of pure toluene, and 81·4 grams of benzene, the loss by evaporation being 22 grams. The total time required was over 30 hours.

Fractional Condensation.—As already discussed, if the whole of a binary mixture is vaporised and then condensed so that the liquid as formed is removed from contact with the residual vapour, this vapour will become progressively richer in the more volatile component, and in this way can be made to reach practically the composition of the pure component. But the yield is relatively very small, since all the mixture has to be vaporised and condensed to get the last residual vapour as the pure constituent. Fractional condensation is nevertheless employed in technical practice, as will be discussed later.

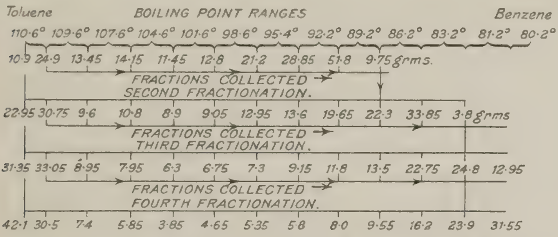


FIG. 4.—Systematic Distillation: Toluene and Benzene.

Fractional Distillation and Condensation.—We see from the above that it is possible by fractional distillation to isolate from a mixture some of the less volatile component in a pure state and by further fractionation some of the more volatile liquid. Also by fractional condensation it is possible to obtain a residual vapour which is practically the pure, more volatile, component. Neither process alone can conveniently yield both the pure components. But if the two processes are carried out simultaneously and repeatedly, separation can be effected very readily provided that the boiling points of the two pure liquids are sufficiently far apart. Such a combined operation is effected in a fractionating column and is termed fractionation, although it is perhaps better known simply as fractional distillation, since distillation is the primary essential. Separation of the components of a liquid mixture by fractionation can be effected either discontinuously or continuously. Since more use is made of discontinuous fractionation, it will be considered first.

---

[1] Unless otherwise indicated, all temperatures are on the Centigrade scale.

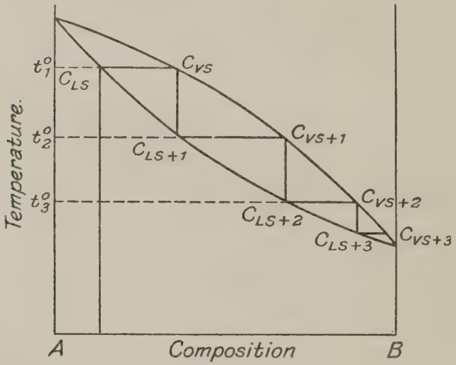


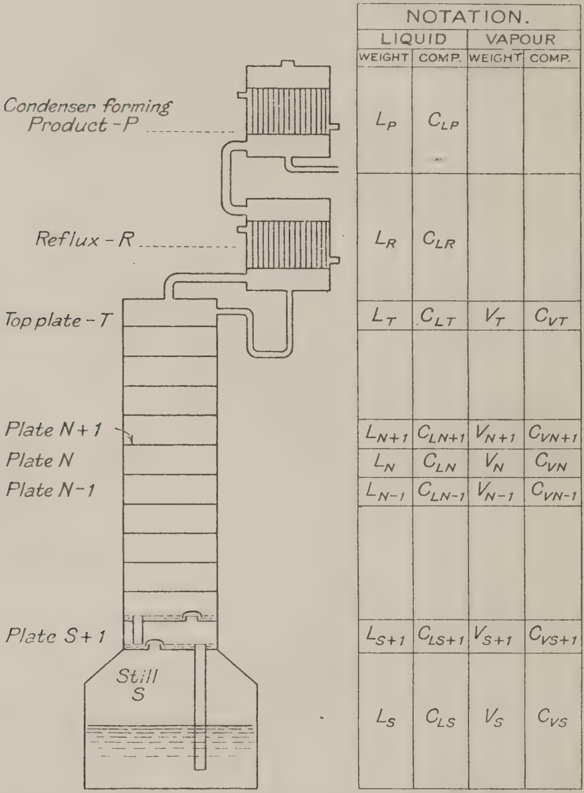
FIG. 5.—Boiling Point–Composition Curve.

Fractionation in Theory.—The theory underlying fractionation can be stated as follows. Consider the boiling point–composition curve, Fig. 5. A mixture of composition C_{LS} boils at t°_1, and the vapours evolved, which are also at t°_1, have a composition C'_{VS}. If these vapours are condensed entirely, their composition will be $C'_{LS\cdot 1}$, which is the same as C'_{VS}, except that it refers to the liquid or boiling-point curve and also the condensed vapours are at t°_2. If these condensed vapours of composition $C'_{LS\cdot 1}$ and at t°_2 are boiled, the vapours evolved have a composition $C_{VS\cdot 1}$. When condensed, their composition is $C'_{LS\cdot 2}$, and, on boiling, the vapours evolved have a composition $C'_{VS\cdot 2}$. It is the same for the other steps in Fig. 5.

But if the vapours of composition C_{VS} and at t°_1 are passed into a mixture of the same composition, but at t°_2, which is less than t°_1, then these vapours are condensed in the liquid, give up their latent heat to it, and therefore cause it to boil. These new vapours of composition $C'_{VS\cdot 1}$ and temperature t°_2 can boil a liquid of composition $C'_{LS\cdot 2}$ and temperature t°_3, and so on for the other steps in the figure. Theoretically, if these distillations and condensations are repeated as many times as the number of steps required to go from an original composition C'_{LS} to pure B, the last vapour would be the more volatile component in a pure state.

Now consider Fig. 6, which represents an apparatus for discontinuous distillation. This apparatus consists of (1) a still containing the charge of original mixture; (2) a column divided into a number of compartments by horizontal plates so constructed that the vapours from the still can pass into the lower compartment and the vapours from one compartment can pass through to the next higher, while the liquid on the plates can only descend by overflowing down a pipe sealed at the bottom by the liquid on the plate below or in the still, as the case may be; (3) a reflux or partial condenser, and (4) a final condenser which converts the final product from vapour to liquid.

Notation Used.—The notation used in Fig. 5 and Chapter I can now be explained and is indicated on the diagram. Each symbol is the initial letter of the name of the thing for which it stands. This system of notation has the important advantage of clarity and avoidance of confusion. (This notation is that adopted



NOTATION.			
LIQUID		VAPOUR	
WEIGHT	COMP.	WEIGHT	COMP.
L_P	C_{LP}		
L_R	C_{LR}		
L_T	C_{LT}	V_T	C_{VT}
L_{N+1}	C_{LN+1}	V_{N+1}	C_{VN+1}
L_N	C_{LN}	V_N	C_{VN}
L_{N-1}	C_{LN-1}	V_{N-1}	C_{VN-1}
L_{S+1}	C_{LS+1}	V_{S+1}	C_{VS+1}
L_S	C_{LS}	V_S	C_{VS}

FIG. 6.—Diagram of Discontinuous Still, showing Notation

by E. H. Leslie, "Motor Fuels," 1923.) *Each equation or expression can be readily expanded into words as it is read because of the ease with which initial letters are associated with the words for which they stand.* Only the following need be remembered :—

C always stands for a composition expressed in terms of the more volatile component and as a decimal part of unity. Physical units of weight and not mols. are referred to. Except when used for subscripts,

L always stands for a weight of liquid.

V always stands for weight of vapour.

Subscripts :

Subscripts of L or V indicate the point in the apparatus where the particular weight of liquid or vapour is located.

Subscripts of C consist of two parts, first, a letter L or V, indicating whether the composition is that of liquid or vapour, and second, letters S, N, R, P, etc., indicating the location of the liquid or vapour whose composition is referred to, as still, n^{th} plate, reflux, product.

Other Symbols :

Symbols M_A, M_B, etc., stand for the molecular weight of the component indicated by the subscript.

Symbols h_a and h_b stand for the latent heats per unit weight of substances A and B respectively.

Discontinuous Fractionation.—Bearing in mind Fig. 5 and the discussion in connection therewith, suppose that there is in the still a charge of weight L_S, of composition C_{LS}, and at t°_1, on plate $S + 1$ a liquid of composition C_{LS+1}, and at t°_2, on plate $S + 2$ a liquid of composition C_{LS+2} and at t°_3 and so on corresponding to the steps in Fig. 5. If a continual supply of heat is maintained to the liquid in the still, the charge of composition C_{LS} evolves vapours of composition C_{VS} and temperature t°_1. These vapours pass into the liquid on the plate $S + 1$, are condensed and by giving up their latent heat cause it to boil. The vapours evolved from the liquid on this plate have a composition C_{VS+1}, and pass into and boil the liquid of composition C_{LS+2}, which evolves vapours of composition C_{VS+2}, and so on from plate to plate, the boiling in each case being due to the fact that although the vapours bubbling into the liquid on a plate above have the same composition as this liquid, yet they are at a higher temperature. We see that the vapours from consecutive plates are progressively richer in the more volatile component B, just as was predicted by the steps in the boiling point–composition curve in Fig. 5.

As, however, the mixture in S distils, it becomes poorer in B, because the vapours are richer in this component than the charge. As the liquid on plate $S + 1$ distils, it also becomes poorer in B, in spite of the fact that it is receiving the vapours from S because C_{VS+1} is greater than C_{LS+1}, and therefore than C_{VS}, since C_{LS+1} equals C_{VS}. If, then, there are as many plates in the column as there are steps to go from a composition C_{LS} to pure B, the vapour from the last plate may be pure B at the start, but becomes poorer in B as distillation proceeds. To make allowance for this change in composition, the number of plates must be increased until they equal the number of steps required to go from pure A to pure B in Fig. 5. In this case, the extra top plates can be assumed to be filled at the start with pure B, but at the end only the top plate would be so filled.

Reflux.—But if the liquid on plate $S + 1$ flows continuously down through the sealed pipe, the composition of the liquid will be changed at a slower rate while the mixture in S will be enriched and also change its composition at a slower rate. In the same way, the liquid on each of the other plates can flow down on to the plate below, so that the rate of change of composition in these trays is retarded. To maintain this flow, part of the vapours from the top plate are condensed and run back on to this plate, a matter which will be discussed later.

Fractionation in Practice.—Unfortunately, the theoretical process described, based on the assumption that the composition changes correspond to the steps in Fig. 5, cannot be realised in practice. The vapours ascending from the still to the first plate and those rising from one compartment to another are not completely condensed in the liquid on the plates above. Also, as the vapours bubble through the liquid and burst at the surface they cause a certain amount of entrainment of the liquid as they ascend into the next plate. Finally, in the still itself the boiling is usually vigorous, much more than would be the case under the conditions of the experimental work from the results of which the boiling point–composition curve is drawn. The vapours are evolved at a rapid rate and are poorer in the more volatile component than would be the case if complete equilibrium were attained. By conducting the operation at a reduced speed, an improvement can be obtained in these respects and therefore in the ease of separation, but as output is thereby reduced, it is not usually found economical to work in this way.

Although the boiling point–composition curves are for equilibrium conditions which are approached but not reached in a technical column, they can still be used to demonstrate in a reasonably approximate manner the progress of the fractionation. Reference to Fig. 1 and to the discussion regarding the use of this figure in establishing the relative proportions of liquid and vapour when a liquid mixture is partly distilled or a binary mixture of vapours is partly condensed reminds us that

$$\frac{\text{Weight of residue}}{\text{Weight of vapour}} = \frac{\text{lineal distance } C'_{VS}O}{\text{lineal distance } C'_{LS}O}.$$

Now consider Fig. 7, the boiling point composition curve of the same pair of liquids as shown in Fig. 5. Each of the horizontal lines represents a plate in a column with the exception of the top one, which represents the still. The still delivers a vapour of composition C_{VS} which is fractionally condensed in the liquid on the first plate, *i.e.*, part of it is condensed and the remainder passes through as vapour. The uncondensed vapour has, however, become enriched in B, its composition being C_{VS+1} while that of the condensed vapour is C_{LS+1}, the liquid on the plate being assumed to have the same composition as the condensed vapour, an assumption that was also made when complete condensation of the uprising vapour in the liquid above was considered. Moreover, in accordance with the arguments in Chapter I to which reference is made in the previous paragraph, the ratio of the condensed to the uncondensed vapour is $C_{VS+1}O_1/C_{LS+1}O_1$. If the composition of the liquid on the plate $S + 1$ is C_{LS+1} as assumed, the vapours evolved have the same composition C_{VS+1} as that of the uncondensed vapours from the still

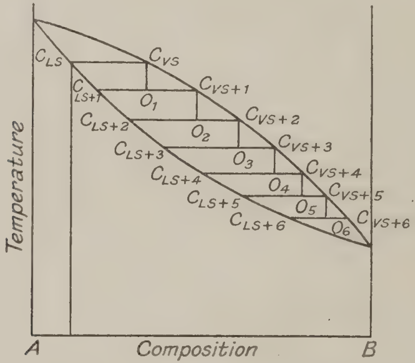


FIG. 7.—Fractionation Diagram.

passing through the liquid. The combined vapours from the first plate pass into the liquid on the second plate, where they are fractionally condensed, and so on from plate to plate as shown diagrammatically in Fig. 7.

Again, the tendency for the liquid in the still and on the various plates to become poorer in B is retarded by allowing the liquid on each plate to flow down on to the next and that on the bottom plate to flow into the still. Thus the liquid on the seventh plate has the composition $C_{LS:7}$ and flows down on to plate 6, where it is fractionally distilled. The vapour evolved from this plate has the composition $C_{VS:6}$, and so on down the column. To maintain this flow, the condenser liquefies part of the vapours from the top plate as previously described.

We see, then, that in a column the two processes, fractional condensation and fractional distillation, are carried out continuously and repeatedly. There are vapours ascending and being fractionally condensed and liquids descending and being fractionally distilled, but these operations are so combined that they are effected by heat interchanges between liquid and vapours. Systematic fractional distillation, on the other hand, involves the successive distillation of condensed distillates, where the heat required for each distillation is lost in the condenser water and, as exemplified earlier in this chapter, the work involved is tedious and on the large scale would be inconvenient and costly. As regards heat interchange, the fractionating column is not unlike a multiple effect evaporator of the counter-flow type with as many effects as there are plates in the column, the main difference being that the vapours mix with the liquid in a column instead of being drawn off as condensate, as is done in the calandria of each effect of a multiple effect evaporator.

The processes that occur in a column are then analogous to those in the ideal and theoretical case, which, however, assumes complete and not fractional condensation and distillation. It is clear that under equal conditions regarding rate of distillation and amount of reflux a greater number of plates is actually required than is theoretically necessary, *i.e.*, the number of steps needed to go from pure *A* to pure *B* in Fig. 5. If it were possible to ascertain the exact amount of fractional distillation and condensation that occurs on each plate for each different pair of liquids, a diagram such as Fig. 7 might be of some value in calculating the number of plates needed. But even though Fig. 7 does give a better diagrammatic representation of the combined processes than Fig. 5, yet the actual conditions in a technical column may be quite different. In both Fig. 5 and Fig. 7 equilibrium conditions between liquid and vapour are assumed, but as such equilibrium requires time to come to completion and as the vapours in works practice travel at a high velocity and are therefore only momentarily in contact with the liquid, the theoretical results are not attained. In addition to the lack of equilibrium, the composition of the liquid may not be uniform at all points on a plate, this defect being naturally more marked in a large column. As a result, the vapours arising from the liquid are not completely uniform. These faults can be largely overcome by careful design and control of the apparatus when working, but are always present more or less. It is therefore necessary to consider the design of a column from the theoretical standpoint, and then to amend the design to suit the particular circumstances, there being a number of points to be considered, such as the cost of steam or other heating medium, the capital cost of the apparatus, and so on. The design of a perfect column for the separation of two components of a binary mixture and the necessary modifications of this design will be discussed later.

Maximum and Minimum Reflux.—It has been mentioned that in order to supply the flow of liquid down the column from plate to plate, part of the vapours from the top plate are condensed and returned to this plate. As explained, this downward flow has the effect of retarding the rate of change of composition of the liquid on each plate and in the still. It is at once obvious that the amount of this reflux will have an influence on the fractionation in the column.

Consider the extreme case of complete reflux, *i.e.*, when all the vapour from the column is condensed and returned. This vapour is richer in B[1] than the liquid on the top plate, and therefore the liquid returned to the top of the column is richer in B than the liquid with which it mixes, so that the proportion of B on the plate increases. The overflow on to the next plate is similarly enriched, and clearly all the other plates are affected in turn. With complete reflux, the weight and composition of the liquid returned to the still from the bottom plate would be the same as the weight and composition of the vapour leaving the still, *i.e.*, $L_{S+1} = V_S$ and $C'_{LS+1} = C'_{VS}$. If, on the other hand, only part of the vapours is liquefied in the condenser, the condensate is poorer and the residual vapours leaving the condenser are richer than the original vapours from the top plate. The enrichment of the liquid on the top plate and therefore on the plates below and finally in the still is not so great as with complete reflux. In this case, C'_{LS+1} is less than C'_{VS}, and as the reflux is decreased so does C'_{LS+1} decrease. Finally, when the reflux is reduced to the theoretical minimum $C_{LS+1} = C_{LS}$.

With complete reflux, the fractionation in the column is a *maximum*, but the vaporisation is also a maximum; in fact, for a given weight of product it is infinite. With minimum reflux, the vaporisation is a *minimum* but the fractionation is a minimum. In actual practice, the reflux lies between the two extreme values C'_{VS} and C'_{LS}. and it is clear that the greater the number of plates in a column, the less will be the reflux needed, and *vice versa*. The designer has to choose between a still with a high capital but low working cost and a cheaper apparatus with higher fuel charges. A compromise has to be effected in order that the final and total working costs per unit weight of product are at a minimum.

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[1] See page 73.

Reflux Ratio.—During the course of a discontinuous distillation the composition of the charge is continually changing and therefore the conditions in the column are also changing. If two liquids, *A* and *B*, are considered, the first vapours from the charge are relatively rich in *B* and consequently the amount of fractionation in the column is small. *The reflux ratio* (*ratio of weight of reflux to weight of distillate in unit time*) is therefore small also. But as the charge becomes weaker in *B* it is necessary to increase constantly the amount of fractionation and therefore the reflux ratio if a constant product is to be obtained. If the rate of evaporation in the still remains the same, the velocity of the vapours up the column will be fairly constant. Therefore the weight of distillate in unit time decreases continuously. When the charge becomes very weak in *B*, the reflux ratio, the amount of fractionation in the column and the amount of evaporation in the still, all per unit weight of product, become excessive and it is preferable to collect an intermediate fraction of a composition much weaker in *B* than the product. When this distillate is thus collected, the residue in the still will be pure *A* and no further distillation is required. The rate of evaporation in the still is usually maintained constant while separating a pure component. If it were changed so that, say, the rate of distillation remained constant, the column would not be worked at its full capacity in the earlier stages.

Intermediate Fractions.—Although it would be advantageous to obtain a complete or nearly complete quantitative separation of the two components of a mixture, it is generally more economical to collect an intermediate fraction as above described. The amount of this fraction need not be large compared with that of the pure distillates, and the fraction is distilled with the next charge, becoming, in fact, a fixed quantity which is not recovered in all similar and subsequent distillations. On the other hand, the amount of this intermediate fraction can be reduced by completely refluxing when the separation becomes difficult. All the distillate from the top of the column is returned to the top plate and the column is entirely engaged in fractionating the liquid in it. Consequently, the upper plates become gradually filled with the pure more volatile component, and if the reflux be now reduced the distillate collected will be for a while the pure constituent *B*. Again, the intermediate fractions from a number of similar distillations may be collected until the total amount of liquid is sufficient to warrant a separate distillation. The procedure in any particular case depends on the circumstances, *e.g.*, the purity of distillate required, the efficiency of the column and so forth.

CHAPTER III

FRACTIONATION (DISCONTINUOUS)

From the previous chapter it will be recalled that in a fractionating column there are vapours ascending and being fractionally condensed and liquids descending and being fractionally distilled, these operations being so combined that they are effected by heat interchanges between liquids and vapours. The ascending vapours become richer and the descending liquids poorer in the more volatile component. In a *perfect* or *ideal* column there would be complete equilibrium between liquid and vapour at all points, and the change in composition would be *continuous* and not in steps as previously considered. To give such a continuous composition change would require a column with an *infinite* number of plates, each of which would produce a *differential* action. In such an ideal process the only heat loss would be in the partial condenser, which returns liquid to form the reflux on to the top plate of the column.

In a commercial column, equilibrium is not attained because it is impossible to provide that intimacy of contact between liquid and vapour necessary to produce the equilibrium, and in addition the time of contact is necessarily too short. The heat loss in an actual operation is greater than in the ideal case because the number of plates is finite and limited. In a commercial column, this limited number of plates has to effect the separation. Consequently the reflux and therefore the evaporation must be increased in order that the fractionating processes on the plates may be repeated a sufficient number of times to give the separation desired.

In the design of equipment and in the conduct of distillation it is necessary to know :—

(1) The minimum weight of vapour that must be formed in the still at any time in order to separate unit weight of product at that time.

(2) The minimum reflux at any time necessary to separate unit weight of product at that time in a column designed to work with no heat loss.

(3) The number of "perfect contacts" between liquid and vapour required to produce a given change in composition at any time and for any weight of reflux.

(4) The number of "imperfect contacts" between liquid and vapour required to produce a given change in composition at any rate and for any given weight of reflux.

Minimum Vaporisation.[1]—Referring to Fig. 6 and using the notation already employed in connection therewith, in order to separate a weight of product L_P from a binary mixture of A and B a weight of vapour V_S must be formed in the still. We have

$$V_S = L_P + L_{S+1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which L_{S+1} is the weight of the liquid returned to the still from the bottom of the column. Considering the more volatile component, we have

$$V_S C_{VS} = L_P C_{LP} + L_{S+1} C_{LS+1} \quad . \quad . \quad . \quad . \quad (2)$$

Eliminating L_{S+1} from (1) and (2), we have

$$V_S C_{VS} = L_P C_{LP} + (V_S - L_P) C_{LS+1} \quad . \quad . \quad (3)$$

As already shown (p. 33), when the reflux is a minimum $C_{LS+1} = C_{LS}$ and for any plate N, $C_{LN+1} = C_{LN}$, *i.e.*, the fractionation from one plate to another is zero. When there is complete reflux $L_{S+1} = V_S$ and $C_{LS+1} = C_{VS}$. If we call V'_S the minimum weight of vapour which must be formed in the still in order to separate a weight of product L_P, then this minimum is attained when the reflux is a minimum, *i.e.*, when $C_{LS+1} = C_{LS}$. Substituting this value of C_{LS+1} in (3), we get

$$V'_S = \frac{L_P(C_{LP} - C_{LS})}{C_{VS} - C_{LS}} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

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[1] Leslie, *Motor Fuels*, 1923.

This applies, of course, only to an ideal apparatus, with an infinite number of perfect contacts, for in any commercial apparatus, the weight of liquid vaporised in the still is necessarily greater than this calculated value of V'_S.

Minimum Weight of Reflux.—For economical working in any given column the loss of heat in the reflux must be reduced to a practical minimum. From equation (1) we have

$$L'_{S+1} = V'_S - L_P,$$

where L'_{S+1} is the minimum weight of liquid returned to the still from the bottom of the column and V'_S is the minimum vaporisation calculated from (4) above.

The minimum reflux L_R returned from the condenser to the top of the column cannot be calculated without taking into account the thermal quantities involved in the composition changes in the column. An exact analysis requires data which are not available and is so involved as to be impractical. In the following, latent heats only are considered, the use of which enables the *approximate* value of any L_R to be calculated. In some cases it is also necessary to take into account the heat of chemical reactions, but the error involved in considering only latent heats is in probably the majority of cases well within the reasonable limits of accuracy in the design of commercial columns.

Equating weights of vapours and liquids entering and leaving the column (see Fig. 6)

$$V_S + L_R = V_T + L_{S+1} \quad . \quad . \quad . \quad . \quad (5)$$

Equating latent heats of vapours entering and leaving the column

$$V_S C_{VS} h_b + V_S(1 - C_{VS})h_a = V_T C_{VT} h_b + V_T(1 - C_{VT})h_a \quad . \quad . \quad . \quad (6)$$

approximately, in which it will be recalled h_b = latent heat per unit weight of the more volatile component B and h_a = latent heat per unit weight of the less volatile component A. These latent heats are to be taken at the approximate mean temperature in the column.

But $$V_T = L_P + L_R \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Combining (6) and (7) and solving for L_R we get

$$L_R \underset{\text{approx.}}{=} \frac{V_S[C_{VS}(h_b - h_a) + h_a]}{C_{VT}(h_b - h_a) + h_a} - L_P$$

and since C_{VT} equals C_{LP} (see p. 73)

$$L_R \underset{\text{approx.}}{=} \frac{V_S[C_{VS}(h_b - h_a) + h_a]}{C_{LP}(h_b - h_a) + h_a} - L_P \quad . \quad . \quad (8)$$

Equation (8) is general and may be applied in ascertaining the value of L_R in the commercial as well as in the ideal column. It may be applied equally well when substances form perfect solutions (such as closely related liquids) or when they do not form such solutions. In the case of perfect solutions the following relationships must hold:

$$L_R \underset{\text{approx.}}{=} \frac{V_S[C_{VS}(M_A - M_B) + M_B]}{C_{LP}(M_A - M_B) + M_B} - L_P \quad . \quad . \quad (9)$$

where M_A and M_B stand for the molecular weights of A and B respectively.

Equation (9) is somewhat more convenient than (8) since molecular weights are known even though latent heats may not be. However, equation (9) can only be used in the case of perfect solutions. When data are available equation (8) is preferable to (9) because (9) assumes that the molecular latent heats of A and B are equal.

If the minimum weight of reflux L'_R is required, it may be found by substituting the minimum vaporisation V'_S for V_S in either (8) or (9).

Composition Change per Unit Section.—In the design or operation of any column, it is necessary to know the change in composition of liquid and vapour that occurs in any unit section of the column as well as in the entire column composed of any number of unit sections. A column section may be any number of plates of any type, as, for example, bubbler or bell type, perforated plate type, or it may be any arbitrarily chosen length of a packed or filled column. The column consisting of a number of sections in which equilibrium is established between vapour and liquid will first be considered and then the commercial column will be discussed in which equilibrium is not attained.

The column-section that produces the same change in the composition of vapour and liquid as is produced in one where perfect contact, and therefore perfect equilibrium, is attained will be designated as a "perfect" column-section or, for brevity, as a "perfect" section.

The symbol dC will be used to indicate the increment of change in composition from one section of the column to the next. The subscripts L or V indicate whether the symbol refers to liquid or vapour. Thus dC'_{LN} refers to the increment of change in composition of the liquid as a result of contact of liquid with vapour in the Nth section.

An exact relationship from which dC'_L in any section of the column can be calculated is derived by equating the weights of materials entering and leaving suitably selected portions of the distillation system. The method is illustrated in the following, where it should be noted that the weight balances are so chosen that the final expression contains only known or calculable weights or compositions. Also discontinuous distillation only is considered in an apparatus similar to Fig. 6.

Consider the column to be cut between sections N and $N+1$. Then, equating weights of materials,

$$V_N = L_{N+1} + L_P \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Equating weights of the more volatile component,

$$V_N C_{VN} = L_{N+1} C_{LN+1} + L_P C_{LP} \quad . \quad . \quad . \quad . \quad (11)$$

By definition of dC above,

$$dC_{LN} = C_{LN+1} - C_{LN} \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Combining (11) and (12) to eliminate C_{LN+1},

$$V_N C_{VN} = L_{N+1}(C_{LN} + dC_{LN}) + L_P C_{LP}.$$

Solving for dC_{LN},

$$dC_{LN} = \frac{V_N C_{VN} - L_P C_{LP}}{L_{N+1}} - C_{LN} \quad . \quad . \quad . \quad (13)$$

Combining (10) and (13) to eliminate L_{N+1}.

$$dC_{LN} = \frac{V_N(C_{VN} - C_{LN}) - L_P(C_{LP} - C_{LN})}{V_N - L_P} \qquad (14)$$

In equation (14) L_P, C_{LP} and C_{LN} are known. For the perfect column section C_{VN} is also known, for it is the composition of the vapour in equilibrium with the liquid in the Nth section. V_N may be assumed, but more commonly L_R per unit weight of L_P, *i.e.*, the reflux ratio is assumed and V_N approximately calculated by taking into account heat quantities as in equation (8). The relationship applicable in this case is

$$V_N \underset{\text{approx.}}{=} \frac{(L_R + L_P)[C_{LP}(h_b - h_a) + h_a]}{C_{VN}(h_b - h_a) + h_a} \quad . \quad . \quad (15)$$

The approximate equation (15) may be derived by substituting C_{VN} for C_{VS} and V_N for V_S in equation (8) and solving for V_N.

When the two liquids form perfect solutions it follows from equation (9) that equation (15) may be written

$$V_N \underset{\text{approx.}}{=} \frac{(L_R + L_P)[C_{LP}(M_A - M_B) + M_B]}{C_{VN}(M_A - M_B) + M_B} \quad . \quad (16)$$

Number of Perfect Sections Required.—In the above a method has been formulated for calculating the composition change in one perfect column-section. The relationship of dC'_{LN} to known weights of liquids and vapours in any section N is given by equations (14) and (15). The general problem of calculating the number of perfect column-sections required to produce any desired change in composition in the case of two components when operating with a given reflux ratio can now be solved. The method is best illustrated by a specific problem.

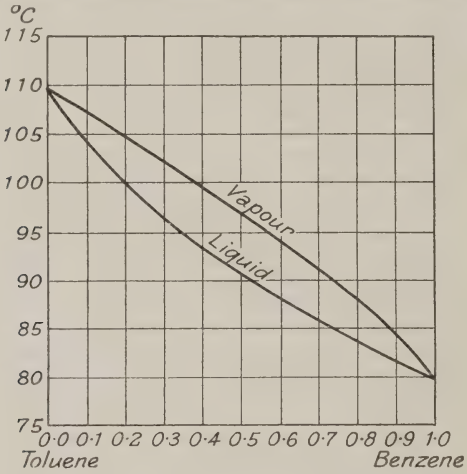


Fig. 8.—Boiling Point–Composition Curve Benzene-toluene at 750 mm.

Discontinuous Distillation Problem.—A mixture of benzene and toluene is to be distilled in such a manner as to give a product containing 95 per cent. of benzene by weight. At the instant when the liquid in the still contains 20 per cent. of benzene and 80 per cent. of toluene by weight, it is desired to know the minimum number of perfect column-sections required if the reflux ratio is 4. Pressure throughout the system is assumed to be 750 mm. of mercury.

The first step is the construction of the boiling point - composition curve as shown in Fig. 8. The first and second columns in Table I give the equilibrium values of liquid and vapour as read from these curves. *The second step* is to calculate value of V_N corresponding to arbitrarily selected values of C_{VN}. For this purpose, appropriate values are substituted in equation (15) or (16). In this instance, equation (16) is used, since benzene and toluene are closely related liquids and form a perfect solution. The following illustrates the method of making the calculation :

TABLE I

C_{LN}.	C_{VN}.	V_N.	dC_{LN}.	$\frac{1}{dC_{LN}}$
0·20	0·375	5·48	0·0467	21·37
0·25	0·445	5·42 [1]	0·0806	12·42
0·30	0·508	5·36 [1]	0·1080	9·27
0·40	0·620	5·26	0·1424	7·03
0·50	0·714	5·19 [1]	0·1574	6·36
0·60	0·792	5·126	0·1538	6·50
0·70	0·857	5·07 [1]	0·1340	7·47
0·80	0·913	5·027	0·1038	9·64
0·90	0·960	4·99 [1]	0·0626	15·98
0·95	0·980	4·978	0·03757	26·62

[1] Read from $C_{LN} \sim V_N$ curve, Fig. 9.

The first arbitrarily selected value of C_{VN} is 0·375, corresponding to a liquid composition of 0·20, *i.e.*, the composition of the liquid in the still. We have from equation (16)

$$V_N = \frac{(L_R + L_P)[C_{LP}(M_A - M_B) + M_B}{C_{VN}(M_A - M_B) + M_B}$$

$$= \frac{(4 + 1)[0{\cdot}95(92 - 78) + 78]}{0{\cdot}375(92 - 78) + 78} = 5{\cdot}48$$

Four similar calculations to this enable the $C_{LN} \sim V_N$ curve in Fig. 9 to be drawn, and from that curve five other values of V_N can be read off. These ten values of V_N, corresponding to values of C_{VN} shown in the second column of Table I, are then inserted in the third column of this table.

The third step is to calculate values of dC_{LN} corresponding to the values of C_{LN} in Table I by substituting proper values in (14)

$$dC_{LN} = \frac{V_N(C_{VN} - C_{LN}) - L_P(C_{LP} - C_{LN})}{V_N - L_P}$$

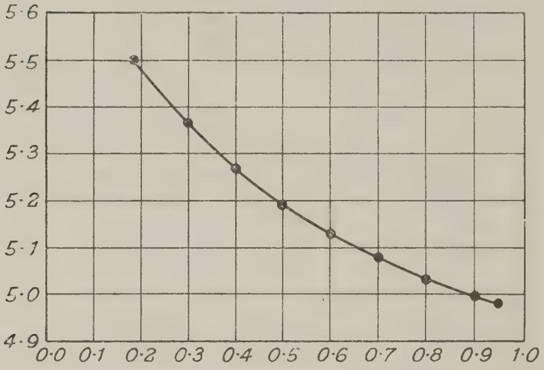


FIG. 9.—$C_{LN} \sim V_N$ Curve.

For the perfect section in which the composition of the liquid is 0·20,

$$dC_{LN} = \frac{5{\cdot}48(0{\cdot}375 - 0{\cdot}20) - 1{\cdot}00(0{\cdot}95 - 0{\cdot}20)}{5{\cdot}48 - 1{\cdot}00} = 0{\cdot}0467.$$

The values shown in column 4 of Table I were calculated in this way.

The values of dC_{LN} are the changes in composition in one perfect section of a column. The reciprocals of these values are the number of perfect column-sections required to produce unit change in liquid composition at the point in the column where, in one section, the composition of the liquid changes from C_{LN} to $C_{LN} + dC_{LN}$ when the composition of the product is C_{LP}. The values of $1/dC_{LN}$ are shown in the fifth column of Table I.

The fourth step is the graphical integration of $C_{LN} \cdot \frac{1}{dC_{LN}}$ between the desired limits which in this problem are 0·95, the composition of the product and 0·20, the composition of the liquid in the still. To do this, the curve shown in Fig. 10 is drawn. Horizontal lines are drawn of length dC_{LN}, corresponding to the selected values of C_{LN} and at distances from the horizontal axis equal to the corresponding value of $1/dC_{LN}$. The abscissæ of the ends of each horizontal line are thus C_{LN} and $(C_{LN} + dC_{LN})$. The smooth curve shown in Fig. 10 is so drawn that the area under the curve between the abscissæ corresponding to the ends of any of the horizontal lines is equal to the area under that horizontal line. The area under any of the horizontal lines is a rectangle whose dimensions are dC_{LN} and $1/dC_{LN}$ and whose area is therefore 1·0. The curve shown in Fig. 10 is

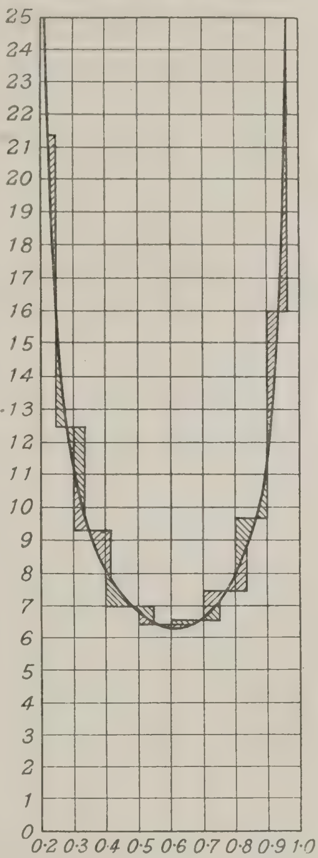


FIG. 10.—Integration Curve for $\frac{1}{dC_{LN}} \cdot C_{LN}$.

so drawn that the similarly shaded areas above and below any horizontal lines are equal. It should be noted that only occasionally will the smooth curve bisect a horizontal line. A planimeter will be found most helpful in constructing the smooth curve.

The value of the desired integral is the area bounded by the smooth curve, the horizontal axis and the ordinates drawn through abscissæ 0·20 and 0·95. The smooth curve has not been extended to intersect the ordinate 0·20, as this was in this instance both inconvenient and unnecessary, since the area under the smooth curve between the abscissæ 0·2 and (0·2 + 0·0467) must be 1·0. The area under the curve between abscissæ 0·2467 and 0·95 is 6·005. The total area is 7·005, and therefore the number of perfect sections required to change the composition from 0·20 to 0·95 is seven. As has been noted, one of these sections is the still itself, and therefore the number of perfect sections in the column is six.

The foregoing discussion exemplifies the method of attacking the general problem of the design of apparatus for discontinuous distillation, but as the composition of the liquid in the still changes continuously, it is desirable to make other calculations, similar to that given in detail above, for *several* successive compositions of the still liquid. The column may be designed to operate with any reflux ratio greater than the minimum for any composition of the liquid in the still. The larger the reflux ratio the smaller the number of perfect sections required to effect any desired separation. Hence for each of the several compositions of the still liquid it is desirable to calculate the number of perfect column-sections for each of a series of assumed reflux ratios. The designer can then select the number of perfect sections for the column and specify the smallest reflux ratio that can be used for any composition of the still liquid. As already discussed (p. 34), complete separation of the components of a binary mixture is not desirable, for it is more economical to collect an intermediate fraction.

The calculations made in the above way give the design of the column as regards the number of perfect sections but not as regards its capacity. The capacity or cross-sectional area is determined by the weight of product to be made in unit time. The weight of product and the largest reflux ratio determine, not only the cross-sectional area of the column, but also the area of the heating surface in the still, the cooling surface of the reflux and final condensers and the sizes of the vapour and liquid pipes.

The Working Column.—As equilibrium is not attained at any point in a working column, this column must be composed of more sections than the perfect column. Some number of plates or unit lengths of the working column will produce the same change in composition as one perfect column-section. This equivalent number is not always the same, but is dependent on the velocity of vapour and liquid in the column and the rate of diffusion of the components, these variables being affected in their turn by the temperature and pressure. Unfortunately, there is very little available information establishing the relationship between the perfect column section and the plate or unit length of commercial columns.

W. A. Peters (*J. Ind. Eng. Chem.*, 1922, **14**, pp. 476–9) gives the results of his experiments, which indicate that when a mixture of acetic acid and water is distilled in a 28-inch diameter column with perforated plates 28 in number, the number of plates equivalent to one perfect column-section is nearly the same as when this solution is distilled through a $4\frac{7}{8}$-inch bell plate column of 20 plates with one bell on each plate, the numbers being 1·92 and 2·2 plates respectively. When a solution of alcohol and water was distilled in one instance through a 36-inch Badger bell plate column and in another through a $4\frac{7}{8}$-inch bell plate column, the plates equivalent to one perfect-section were 1·43 and 1·44 respectively.

Peters also gives the results of experiments conducted to determine the length of ring-packed laboratory column equivalent to one perfect column-section. His results are shown in Table II.

TABLE II

Lengths of Ring-packed Laboratory Column equivalent to one Perfect Column-section.

System distilled.	Height of column equivalent to one perfect column-section. Inches.
Ethyl alcohol–water, with more than 88% alcohol	4·2
Ethyl alcohol–water, with less than 88% alcohol	3·65
Ethyl alcohol–water, dilute residue almost pure water	3·87
Methyl alcohol–water	3·0
Acetone–ethyl alcohol	6·0
Nitric acid–water	8·0
Nitric acid–water–sulphuric acid . .	3·75
Acetic acid–water	10·00
Benzene–toluene	10·00
Ammonia–water residue almost pure water	3·4

It is evident that until data become available dealing with the relationship between the perfect column and the working column the method described is of rather limited practical utility. That is, however, no reason why the study should not be continued. The limitation of the discussion to two components is a further disadvantage, for fractional distillation is by no means confined to the separation of such simple mixtures. In many industries the initial mixtures are exceedingly complex, and it would be manifestly impossible to ascertain either by calculations or by graphical methods the size of column, the amount of reflux and other necessary information. Again, fractional distillation is often employed to separate the components of a mixture from the impurities contained therein, and in such cases also the principles described would not be applicable.

On the other hand, it frequently happens that a mixture is composed mainly of two components, the other constituents being present in relatively small amounts. In this case, the design can be approached from the standpoint of a two-component system and modifications introduced to make provision for the other components. When the same kind of mixture is constantly being distilled in fairly large quantities, it is useful, and very often valuable to evolve the data for the perfect column as described. By comparing the calculated and actual results it is possible to amass information which can be applied to obtain noticeable improvement in the method of working, and therefore in economy or ease of separation or both. Further, from this experience and data any additional apparatus or any plant installed to replace that worn out can be designed with a much more intimate knowledge of the "inner working" than would otherwise be available. Unfortunately, in a great many works the distillation methods employed are often of the very crudest nature, with practically no consideration for the fundamental principles. The control of the working of the still is left in the hands of the workman, who gradually acquires sufficient intimacy with the mixture in question to produce the desired products in a reasonably economical, sometimes in a very economical manner. But this experience is not available for any possible improvement in either method or design.

Lewis's Method.—The method used by W. K. Lewis as described by Robinson ("Elements of Fractional Distillation," 1922, p. 53) in the case of intermittent distillation can be given here in a brief form, using the previous notation and equations.

For the Nth plate per unit time we have (combining (10) and (11) to eliminate V_N)

$$L_{N+1} = \frac{L_P(C_{LP} - C_{VN})}{(C_{VN} - C_{LN+1})} \quad . \quad . \quad . \quad . \quad . \quad (16\text{A})$$

As already shown (p. 37), when there is minimum reflux the fractionation is zero and $C_{LN+1} = C_{LN}$. Therefore the minimum reflux for unit weight of product ($L_P = 1$)

$$L'_{N+1} = \frac{C_{LP} - C_{VN}}{C_{VN} - C_{LN}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (16\text{B})$$

Combining equations (16A) and (12) we have (omitting the intermediate calculations),

$$dC_{LN} = C_{VN} - C_{LN} - \frac{C_{LP} - C_{VN}}{L_{N+1}} \quad . \quad . \quad (16\text{C})$$

which gives the increment of change of composition of the liquid as a result of contact of liquid with vapour in the Nth section. This applies to a perfect contact in a perfect column, but the actual rate of concentration will be less than this, so that dC_{LN} (actual) $= k \,.\, dC_{LN}$ (theoretical). Equation (16C) therefore becomes

$$dC_{LN}\,(\text{actual}) = k(C_{VN} - C_{LN}) - \frac{k(C_{LP} - C_{VN})}{L_{N+1}} \quad (16\text{D})$$

The factor k *is, of course, the relationship between the perfect and the working column and must be known in each case under consideration.* Lewis calls k the plate efficiency. Assuming a reflux greater than the minimum reflux calculated by (16B) the number of plates or contacts can be calculated as before by the graphical integration of $C_{LN} \cdot \frac{1}{dC_{LN}}$ between the desired limits, viz. the composition of the product and that of the liquid in the still.

CHAPTER IV

FRACTIONATION (CONTINUOUS)

In the previous chapters there has been considered the separation of two liquids from each other by discontinuous fractional distillation, a method in which the composition and temperature at any point in the system change continually. In continuous distillation, on the other hand, the conditions at any point are constant, and consequently the apparatus can be run at full capacity at all times, whereas in the intermittent method the changing conditions cause corresponding changes in the working of the plant.

In the continuous still, the mixture, previously preheated either by heat exchange, direct heat or a combination of both, is fed at a constant rate into a column comprised of bell plates, perforated plates or other suitable fractionating devices. In this column the mixture is separated, one component, the more volatile, leaving the top and the other component leaving the bottom. The section into which the feed is introduced is called the "feed-section" or, where plates are employed, the "feed-plate." If a packed column is employed a feed-plate is usually provided to distribute the mixture evenly over the packing. This feed-plate divides the continuous working column into two sections, which can be regarded as two distinct columns. Of these two columns or sections the one below the feed is engaged in separating the less volatile component of the mixture and this constituent flows out at the bottom freed from the more volatile liquid. The designation "exhaustion" or "stripping column" is frequently given to this lower section, due no doubt to its use for the separation of alcohol and water, a mixture in which only the alcohol is of value, the water being merely a residue which is exhausted or stripped of its alcohol content. The upper section or column is often called the "concentration" or "rectifying column," again on account of its employment in alcohol distillation, since the alcoholic vapours are concentrated or rectified in it. The heat necessary for vaporisation is supplied by some suitable heating device at the bottom of the exhaustion column, while the vapour from the concentration section passes to a condenser which returns part of it as liquid to form the reflux on to the top plate, and thence down the column.

The relationships between conditions and quantities which were established for discontinuous distillation in the previous chapter hold, as indicated, only at any particular instant. The operation of the column in a continuous still is complicated by the fact that, while the vapour passing up through the column is the same per unit of time for all parts of that column, the amount of reflux passing in the opposite direction is increased at the feed-plate by the addition of the entering feed. The discussion that follows is concerned with the development of expressions for quantity of feed, minimum vaporisation, weight of reflux and change in composition effected by one perfect column-section located above or below the feed-plate.

Notation Used.[1]—The notation used is the same as before with the following additions or modifications:

> The subscript F refers to the feed, and not to the feed-section.
>
> The subscript N is reserved to designate the feed-section or any section above the feed-section.
>
> The subscript M refers to the "mixing" or feed-section. Sections above and below this may be designated by subscripts $M + 1$, $M + 2$, $M - 1$, $M - 2$, etc.
>
> The subscript B refers to any section below the

---

[1] Leslie, *Motor Fuels*, 1923.

mixing or feed-section. Sections above or below this may be designated by subscripts $B+1$, $B+2$, $B-1$, $B-2$, etc.

It should be noted that reference may be made to some sections in the column by more than one subscript. Fig. 11 shows the notation diagrammatically.

Quantity of Feed and Residue.—Equating the weights of feed and of product and residue from the column

$$L_F = L_P + L_S \quad . \quad . \quad . \quad . \quad . \quad (17)$$

Considering the more volatile component,

$$L_F C_{LF} = L_P C_{LP} + L_S C_{LS} \quad . \quad . \quad . \quad (18)$$

Eliminating L_S from (17) and (18),

$$L_F = \frac{L_P(C_{LP} - C_{LS})}{C_{LF} - C_{LS}} \quad . \quad . \quad . \quad (19)$$

Eliminating L_F from (17) and (18),

$$L_S = \frac{L_P(C_{LP} - C_{LF})}{C_{LF} - C_{LS}} \quad . \quad . \quad . \quad (20)$$

$$= L_F - L_P \text{ from (17).}$$

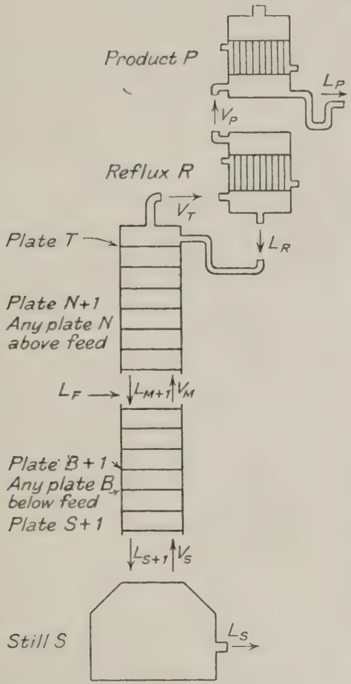
Minimum Vaporisation.—To separate a weight of product L_P from a binary mixture, a weight of vapour V_S must be formed. But since the vapour in this instance is not the source of all the volatile component entering the column, as with intermittent distillation, it is necessary to consider heat quantities as well as weights of volatile component entering and leaving the apparatus in order to formulate a relationship that can be solved for the minimum vaporisation V'_S. This V'_S is found by considering separately the parts of the column above and below the feed-section.

For the part of the column above the feed-section it follows from analogy from equation (4) that

$$V'_M = \frac{L_P(C_{LP} - C_{LM})}{C_{VM} - C_{LM}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

since plate M can be considered as a still charged with liquid of composition C_{LM}.

Equating latent heat of vapours entering and leaving the column below and including the feed section



NOTATION.			
LIQUID		VAPOUR	
WEIGHT	COMP.	WEIGHT	COMP.
L_P	C_P		
L_R	C_R		
L_T	C_{LT}	V_T	C_{VT}
L_{N+1}	C_{LN+1}	V_{N+1}	C_{VN+1}
L_N	C_{LN}	V_N	C_{VN}
L_M also	C_{LM} feed	V_M	C_{VM}
L_F	C_{LF}		
L_{B+1}	C_{LB+1}	V_{B+1}	C_{VB+1}
L_B	C_{LB}	V_B	C_{VB}
L_{S+1}	C_{LS+1}	V_{S+1}	C_{VS+1}
L_S	C_{LS}	V_S	C_{VS}

FIG. 11.—Diagram of Continuous Still, showing Notation.

$$V_S C_{VS} h_b + V_S(1 - C_{VS})h_a = V_M C_{VM} h_b + V_M(1 - C_{VM})h_a$$

whence for minimum vaporisation

$$V'_{S\ \text{approx.}} = \frac{V'_M[C_{VM}(h_b - h_a) + h_a]}{C_{VS}(h_b - h_a) + h_a} \quad . \quad . \quad . \quad . \quad (22)$$

In the case of liquids which form a perfect solution, we can write, as on page 39,

$$V'_S \underset{\text{approx.}}{=} \frac{V'_M[C_{VM}(M_A - M_B) + M_B]}{[C_{VS}(M_A - M_B) + M_B]} \quad . \quad . \quad (23)$$

Combining equations (21) and (22) to eliminate V'_M,

$$V'_S \underset{\text{approx.}}{=} \frac{[C_{VM}(h_b - h_a) + h_a] \,.\, L_P(C_{LP} - C_{LM})}{[C_{VS}(h_b - h_a) + h_a](C_{VM} - C_{LM})} \quad (24)$$

When the reflux is a minimum, the number of perfect sections in the column is infinite and the change in composition from one section to the next is infinitesimal. Therefore $C_{LM} = C_{LF}$ and $C_{VM} = C_{VF}$, for if C_{LM} were not equal to C_{LF}, a finite change in liquid composition in the column would result from the introduction of the feed, and such discontinuity in composition with an infinite number of sections is impossible. Hence

$$V'_S \underset{\text{approx.}}{=} \frac{[C_{VF}(h_b - h_a) + h_a]L_P(C_{LP} - C_{LF})}{[C_{VS}(h_b - h_a) + h_a](C_{VF} - C_{LF})} \quad . \quad (25)$$

Similarly, from (21) and (23),

$$V'_S \underset{\text{approx.}}{=} \frac{[C_{VF}(M_A - M_B) + M_B]L_P(C_{LP} - C_{LF})}{[C_{VS}(M_A - M_B) + M_B](C_{VF} - C_{LF})} \quad (26)$$

Minimum Reflux.—With minimum vaporisation, the weight of liquid returned to the still from the bottom of the column and also the weight of reflux are a minimum. Equating weights of vapour and liquid entering and leaving the apparatus between the bottom of the column and the condenser

$$L'_{S+1} = V'_S + L_F - L_P \quad . \quad . \quad . \quad (27)$$

Combining (25) and (27)

$$L'_{S+1} = \frac{[C_{VF}(h_b - h_a) + h_a]L_P(C_{LP} - C_{LF})}{[C_{VS}(h_b - h_a) + h_a](C_{VF} - C_{LF})} + L_F - L_P.$$

Equations (26) and (27) may be similarly combined to give an expression for the minimum weight of liquid leaving the bottom of the column when perfect solutions are considered .

The minimum reflux weight is found as follows. Equating weights of materials in and out of the reflux,

$$V_T = L_P + L_R \quad . \quad . \quad . \quad . \tag{29}$$

Equating latent heats of the vapours entering and leaving the column as in equation (6),

$$V_S C_{VS} h_b + V_S(1 - C_{VS}) h_a \underset{\text{approx.}}{=} V_T C_{VT} h_b + V_T(1 - C_{VT}) h_a \tag{30}$$

Combining (29) and (30) to eliminate V_T,

$$L_R \underset{\text{approx.}}{=} \frac{V_S[C_{VS}(h_b - h_a) + h_a]}{C_{VT}(h_b - h_a) + h_a} - L_P \quad . \quad . \tag{31}$$

Since $C_{VT} = C_{LP}$,

$$L_R \underset{\text{approx.}}{=} \frac{V_S[C_{VS}(h_b - h_a) + h_a]}{C_{LP}(h_b - h_a) + h_a} - L_P \quad . \quad . \tag{32}$$

It should be noted that the vaporisation (*i.e.*, V_S in (32)) in the continuous still equals $L_P + L_{S+1} - L_F$, whereas in the intermittent type $V_S = L_P + L_{S+1}$.

In the case of perfect solutions,

$$L_R \underset{\text{approx.}}{=} \frac{V_S[C_{VS}(M_A - M_B) + M_B]}{C_{LP}(M_A - M_B) + M_B} - L_P \; . \tag{33}$$

The minimum reflux weight L'_R for the ideal column is found by substituting the minimum vaporisation V'_S calculated from (25) or (26) in either (32) or (33).

Composition Change per Unit Section above Feed.—The changes in the column above the feed-plate correspond to those in a discontinuous still when the liquid composition in the latter is the same as that in the feed-section of the continuous column. Consequently equations (10) to (16) in Chapter II can be rewritten thus :—

$$V_N = L_{N+1} + L_P \tag{34}$$

$$V_N C_{VN} = L_{N+1} C_{LN+1} + L_P C_{LP} \tag{35}$$

$$dC_{LN} = C_{LN+1} - C_{LN} \tag{36}$$

$$dC_{LN} = \frac{V_N C_{VN} - L_P C_{LP}}{L_{N+1}} - C_{LN} \tag{37}$$

$$dC_{LN} = \frac{V_N(C_{VN} - C_{LN}) - L_P(C_{LP} - C_{LN})}{V_N - L_P} \tag{38}$$

$$V_N \underset{\text{approx.}}{=} \frac{(L_R + L_P)[C_{LP}(h_b - h_a) + h_a]}{C_{VN}(h_b - h_a) + h_a} \tag{39}$$

Again, for perfect solutions,

$$V_N \underset{\text{approx.}}{=} \frac{(L_R + L_P)[C_{LP}(M_A - M_B) + M_B]}{C_{VN}(M_A - M_B) + M_B} \tag{40}$$

Exhaustion Column.—In the exhaustion column the reflux from the section above the feed is increased by the amount of the feed. Equating weights of liquid and vapour entering and leaving that part of the column between the sections B and $M + I$,

$$V_B + L_F + L_{M+1} = V_M + L_{B+1} \tag{41}$$

By definition of dC_L (page 40),

$$dC_{LB} = C_{LB+1} - C_{LB} \tag{42}$$

Equating weights of liquid and vapour entering and leaving the apparatus above the Mth section, .

$$V_M = L_{M+1} + L_P \tag{43}$$

Combining (41) and (43) to eliminate L_{M+1},

$$V_B + L_F = L_P + L_{B+1} \tag{44}$$

Considering the more volatile component, then from (44)

$$V_B C_{VB} + L_F C_{LF} = L_P C_{LP} + L_{B+1} C_{LB+1} \tag{45}$$

Combining (42) and (45) to eliminate C_{LB+1} and solving for dC_{LB},

$$dC_{LB} = \frac{V_B C_{VB} + L_F C_{LF} - L_P C_{LP}}{L_{B+1}} - C_{LB} \tag{46}$$

Combining (44) and (46) to eliminate L_{B+1},

$$dC_{LB} = \frac{V_B(C_{VB} - C_{LB}) + L_F(C_{LF} - C_{LB}) - L_P(C_{LP} - C_{LB})}{V_B + L_F - L_P} \quad (47)$$

From definition of subscript *B*, the *B*th section may be any section of the column below the feed-section and may therefore coincide with the still, in which event $C_{LB} = C_{LS}$ and $C_{VB} = C_{VS}$.

Location of Feed Point.—The location of the feed-section in a continuous working column should be such that the number of section required should be a minimum. The position of the feed-section is influenced somewhat by the reflux ratio.

Let the liquid composition in the column at the point at which the feed is introduced be called C_{LX}. When the feed and the liquid flowing down the column are mixed the composition of the mixture is

$$C_{LM} = \frac{L_{M+1}C_{LX} + L_F C_{LF}}{L_{M+1} + L_F}.$$

The number of sections in the column is equal numerically to the area under the $\frac{1}{dC_{LB}} \sim C_{LB}$ curve from C_{LS} to C_{LX} plus the area under the $\frac{1}{dC_{LN}} \sim C_{LN}$ curve from C_{LM} to C_{LP}. (See Fig. 12.) C_{LX} must be so selected that the sum of these areas, and therefore the number of sections in the column, may be a minimum. The composition C_{LX} in most instances is so close to C_{LF} that only a negligible error is involved in introducing the feed into that section of the column where the composition of feed and liquid in the column is equal. If it should appear from the curves showing the reciprocal of the rate of enrichment (Fig. 12) above and below the feed-section that an important error will be introduced by taking

$C_{LF} = C_{LX}$, the value of C_{LX} can be determined graphically in accordance with the above principles, so that the number of plates will be a minimum.

Continuous Distillation Problem.—A mixture of 30 per cent. benzene and 70 per cent. toluene by weight is to be distilled to give a product with 95 per cent. benzene and 5 per cent. toluene and a residue with 10 per cent. benzene and 90 per cent. toluene. What weight of liquid must be fed to the column to make unit weight of product? What is the minimum reflux for the ideal column? How many perfect sections must be in the column above and below the feed-section when the reflux ratio is 4? When the reflux ratio is 6? Where should the feed be introduced? The constant pressure assumed is 750 mm.

(A) *Weight of Feed.*—From equation (19),

$$L_F = \frac{L_P(C_{LP} - C_{LS})}{C_{LF} - C_{LS}} = \frac{1{\cdot}0(0{\cdot}95 - 0{\cdot}1)}{0{\cdot}3 - 0{\cdot}1} = 4{\cdot}25.$$

(B) *Minimum Reflux for Ideal Column.*—Since benzene and toluene form perfect solutions, from (33) we have

$$\begin{aligned} L'_R &\underset{\text{approx.}}{=} \frac{V'_S[C_{VS}(M_A - M_B) + M_B]}{C_{LP}(M_A - M_B) + M_B} - L_P \\ &\underset{\text{approx.}}{=} \frac{V'_S[0{\cdot}203(92 - 78) + 78]}{0{\cdot}95(92 - 78) + 78} - 1{\cdot}0 \\ &= 0{\cdot}886 V'_S - 1{\cdot}0 \text{ approx.} \end{aligned}$$

The value of C_{VS} is that corresponding to $C_{LS} = 10$ per cent. benzene, and is found from the boiling point–composition curve. (See Fig. 8.)

The value of V'_S is found from (26),

$$\begin{aligned} V'_S &\underset{\text{approx.}}{=} \frac{[C_{VF}(M_A - M_B) + M_B] . L_P(C_{LP} - C_{LF})}{[C_{VS}(M_A - M_B) + M_B](C_{VF} - C_{LF})} \\ &\underset{\text{approx.}}{=} \frac{[0{\cdot}508(92 - 78) + 78]1{\cdot}0(0{\cdot}95 - 0{\cdot}30)}{[0{\cdot}203(92 - 78) + 78](0{\cdot}508 - 0{\cdot}300)} \\ &= 3{\cdot}28 \text{ approx.} \end{aligned}$$

Hence $L'_R = (0{\cdot}886 \times 3{\cdot}28) - 1{\cdot}0 = 1{\cdot}91$.

The reflux used in a working column must be greater than this.

(C) *Number of Perfect Sections.* Reflux ratio = 4.

For the concentration column the calculations are identical with those for the intermittent working still (Chapter III). Values of V_N for the chosen values of C'_{LN} are calculated by equation (40) and corresponding values of dC'_{LN} by (38). From the results of a few calculations the $C'_{LN} \sim V_N$ curve similar to Fig. 9 can be drawn and other values of V_N read off. (See bottom of page 43.) The $\dfrac{1}{dC_{LN}} \sim C'_{LN}$ curve can then be drawn like Fig. 10.

The construction of the $\dfrac{1}{dC_{LB}} \sim C'_{LB}$ curve for the exhaustion column is based on values of dC'_{LB} calculated from (47). The value of V_B in this equation may be found from equation (33). From the derivation of (33) it is evident that V_B and C_{VB} may be substituted for V_S and C_{VS}. The results of all the calculations are given in Table III.

TABLE III

Reflux ratio = 4·0.

C_{LN} or C_{LB}.	C_{VN} or C_{VB}.	V_N or V_B.	dC_{LN}.	$\dfrac{1}{dC_{LN}}$.	dC_{LB}.	$\dfrac{1}{dC_{LB}}$.
0·95	0·980	4·98	0·0376	26·6	—	—
0·90	0·960	4·99	0·0626	16·0	—	—
0·80	0·913	5·03	0·1038	9·6	—	—
0·70	0·857	5·07	0·1340	7·5	—	—
0·60	0·792	5·13	0·1538	6·5	—	—
0·50	0·714	5·19	0·1574	6·4	—	—
0·40	0·620	5·27	0·1424	7·0	0·0217	46·1
0·35	0·567	5·32	—	—	0·0407	24·6
0·30	0·508	5·36	0·1080	9·3	0·0541	18·5
0·25	0·445	5·42	0·0806	12·4	0·0660	15·2
0·20	0·375	5·49	0·0467	21·4	0·0730	13·7
0·15	0·293	5·57	—	—	0·0721	13·9
0·10	0·203	5·65	—	—	0·0655	15·3
0·05	0·112	5·75	—	—	0·0576	17·4
0·00	0·000	5·86	—	—	0·0357	28·0

The curves constructed from the data in Table III are those shown dotted in Fig. 12.

Assuming that the composition of the liquid in the column at the point where the feed is introduced is the same as that of the liquid feed = 0·3, the area under the $\frac{1}{dC_{LN}} \sim C_{LN}$ curve between $C_{LN} = 0{\cdot}95$ and $C_{LN} = 0{\cdot}30$ is 5·34 and the area under $\frac{1}{dC_{LB}} \sim C_{LB}$ curve from $C_{LB} = 0{\cdot}30$ to $C_{LB} = 0{\cdot}10$ is 2·89. The total area is the sum of these areas, or 8·23. The perfect sections of the column are thus 8·23, of which the still is one perfect section. The number of perfect sections in the column is therefore 7·23, of which 5·34 are above the feed-section. The number of plates or length of packed column in any working apparatus should be distributed accordingly.

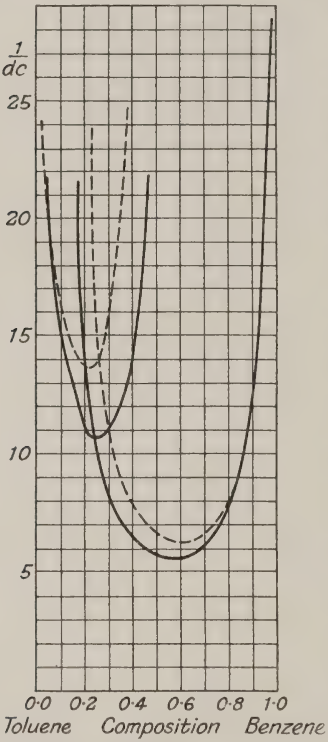


Fig. 12.—$\frac{1}{dC} \sim C_L$ Curve.

(D) *Number of Perfect Sections.*—Reflux ratio = 6.

The procedure is identical with that given in (C). The calculated quantities are given in Table IV and the curves are the solid line curves in Fig. 12. The area under the $\frac{1}{dC_{LN}} \sim C_{LN}$ curve between $C_{LN} = 0{\cdot}95$ and $C_{LN} = 0{\cdot}30$ is 4·86. The area under the $\frac{1}{dC_{LB}} \sim C_{LB}$

curve between $C_{LB} = 0·30$ and $C_{LB} = 0·10$ is 2·37. The total area is the sum of these, or 7·23. The number of perfect sections in the column is 6·23, of which 4·86 are above the feed-section.

TABLE IV

C_{LN} or C_{LB}.	C_{VN} or C_{VB}.	V_N or V_B.	dC_{LN}.	$\frac{1}{dC_{LN}}$.	dC_{LB}.	$\frac{1}{dC_{LB}}$.
0·00	0·000	8·20	—	—	0·0284	36·2
0·03	0·070	8·11	—	—	0·0486	20·6
0·05	0·112	8·05	—	—	0·0586	17·1
0·10	0·203	7·91	—	—	0·0732	13·7
0·12	0·240	7·87	0·0167	60·0	—	—
0·15	0·293	7·80	0·0464	21·6	—	—
0·17	0·327	7·84	—	—	0·0905	11·1
0·20	0·375	7·70	0·089	11·2	0·0935	10·7
0·25	0·445	7·60	0·118	8·5	0·0914	11·0
0·30	0·508	7·53	0·140	7·1	0·0850	11·8
0·40	0·620	7·37	0·168	5·0	0·0606	16·5
0·45	0·668	7·31	—	—	0·0431	23·2
0·50	0·714	7·26	0·176	5·7	0·0237	42·1
0·60	0·792	7·18	0·166	6·1	—	—
0·70	0·857	7·10	0·142	7·1	—	—
0·80	0·913	7·04	0·107	9·4	—	—
0·90	0·960	7·02	0·0616	16·3	—	—
0·95	0·980	7·01	0·0350	28·6	—	—

(E) *Location of Feed.*—The location of the feed has been discussed on p. 59, but it is of interest to compare the application of the method of Lewis (*J. Ind. Eng. Chem.*, 1922, **14,** pp. 496–7) and Robinson ("Elements of Fractional Distillation," 1922, pp. 55–61) as used in the design of continuous working equipment. The reflux below the feed-plate is greater than that above by the amount of the feed. Considering any section or plate B below the feed,

$$L_{B+1} = L_{M+1} + L_F.$$

Equation (16D) on p. 50 does not therefore directly apply in a continuous column to the portion below the feed-plate, but a similar one may be substituted for it, making use of the concentration of the liquor leaving the bottom of the column, which, in accordance with the notation of Fig. 11, is C_{LS+1}. We have

$$dC_{LB} = k(C_{VB} - C_{LB}) - \frac{k(C_{VB} - C_{LS+1})(L_F - 1)}{L_{B+1}} \qquad (16\text{E})$$

(It must be remembered that in the equation $L_P = 1$.) At the point of entrance of the feed into the column plates B and M become identical, and since there must be continuity of operation at this point for smooth working, the rate of change of composition must be the same, *i.e.*, $dC_{LM} = dC_{LB}$. Therefore equations (16D) and (16E) must be equal at the feed-point.

Consequently "the feed should enter the column on that plate at which the enrichment curves for the bottom and top of the column intersect, as otherwise efficiency of utilisation of the plates is sacrificed." The enrichment curves are, of course, those of

$$\frac{1}{dC_{LN}} \sim C_{LN} \text{ and } \frac{1}{dC_{LB}} \sim C_{LB}.$$

Lewis also states that "it would seem that in commercial practice the feed is often introduced too high up the column."

It is of interest to note the difference in the number of perfect sections required when the feed is introduced where its composition equals the composition of the liquid in the column and at the composition represented by the point where the enrichment curves intersect. The corresponding areas or number of perfect sections required in the two cases are shown in Table IV. Inspection of the last column in this table illustrates the point that introduction of the feed at one point or at the other does not greatly influence the number of perfect sections required. In view of this fact and since introduction of the feed at either of these points is to be regarded as a limiting case, there seems to be little object in making an elaborate effort to locate the exact point of entrance.

TABLE V

Data bearing on Location of Feed-section.

AREA OR NUMBER OF PERFECT SECTIONS

Reflux ratio. L_R.	$C_{LX} = C_{LF}$.			$C_{LX} = C_L$ at intersection.			Difference of totals.
	Above feed.	Below feed.	Total.	Above feed.	Below feed.	Total.	
4·0	5·34	2·89	8·23	5·77	2·60	8·37	0·14
6·0	4·86	2·37	7·23	5·32	2·14	7·46	0·23

Temperature of the Feed.—It is desirable that the temperature of the entering feed should be the same as that of the liquid in the column at the point of entrance, and this has been assumed in the foregoing. This condition is not usually fulfilled in practice, and consequently the still has to furnish the heat required to raise the feed to the temperature of the liquid on the feed-plate. Since this heat is provided by condensation of the vapour from the exhaustion column, the weights of liquid and vapour will be somewhat larger than those calculated by the use of the equations in this chapter. The consumption of steam will, of course, be increased. If the feed is not hot enough, allowance must be made for the effect that the relatively low temperature will have.

The Working Column.—In order to apply the results obtained by use of the foregoing equations, it is necessary to know the relationship between the perfect column and the working apparatus. As in the case of discontinuous distillation, the absence of data renders the discussion of limited value at present, but, on the other hand, the methods outlined can be used in continuous distillation to give the ratio between the number of plates or length of packed column above and below the feed-point in the working apparatus. The effect of changing the reflux can also be ascertained and can be of considerable service.

Intermittent and Continuous Distillation.—The relative advantages and disadvantages of the intermittent and continuous systems of distillation are given below in tabular form.

INTERMITTENT STILLS

Advantages.

(1) Simple in design and construction.

(2) Capital cost is less than for the continuous type.

(3) Often adaptable for use with other mixtures than those for which they were originally made.

(4) More suitable for small-scale work where quality and quantity of the materials to be distilled may be subject to frequent change.

Disadvantages.

(1) The concentration changes continuously and progressively with the distillation, necessitating a continuous change in the reflux ratio to give the desired separation. The rate at which the product is delivered varies with the amount of fractionation required to effect separation.

(2) The heat required to raise the mixture to the boiling point is lost. In the case of simple distillation where no fractionating column is employed, the vapours from the still may be used to preheat and even to distil partly the next still charge by passing the vapours through a preheater containing the cold mixture and placed between the still and the condenser.

(3) Considerable heat is lost through the production of intermediate fractions, which must be redistilled.

(4) Additional labour is required for the redistillation of these intermediate fractions.

(5) The filling, emptying and cleaning involve labour and time.

CONTINUOUS STILLS

Advantages.

(1) Uniform and high-grade product.

(2) High rate of working.

(3) Regularity of operation.

(4) Heat economy due to possibility of heat interchange and to avoidance of intermediate fractions which require subsequent redistillation.

(5) No labour required for redistillation of intermediate fractions and for filling, emptying and cleaning.

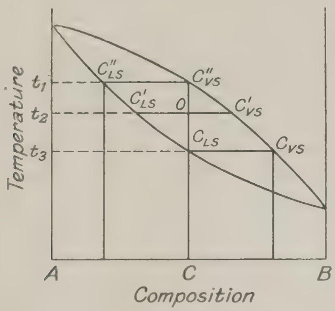


FIG. 13 (see page 69)

Disadvantages.

(1) High first cost due to the numerous accessories that are required to ensure automatic operation, in spite of the fact that there is no large vessel, such as is necessary in discontinuous distillation, to hold the charge.

(2) Complicated construction and operation. Later in this book examples are given showing the construction. The operation requires fairly skilled labour.

(3) Not usually adaptable for mixtures other than those for which originally designed.

(4) Sensitiveness to external conditions. The amount

and composition of the feed, the steam supply for heating and the water supply for condensation must be kept uniform.

The intermittent type is much more popular than the continuous type, which can only be employed where large and regular quantities of liquor have to be treated such as are found in the oil-fields, etc. Where its installation is warranted, however, continuous working is much to be preferred.

CHAPTER V

FRACTIONAL CONDENSATION

In the previous chapters fractional distillation was discussed as a means of separating the components of a mixture. The fractionation process was seen to be composed of the two individual processes, fractional distillation and fractional condensation, which proceed *pari passu* in the fractionating column and which, in their turn, can be regarded as comprising simple distillation and condensation repeatedly performed. Fractional condensation *per se* can, however, be employed to effect separation, the whole of a given mixture being evaporated and condensed in fractions. We can consider two types of fractional condensation as follows.

Equilibrium Condensation.—In Chapter I it was shown that if a binary vapour mixture of composition C''_{VS} (Fig. 13) is condensed under such conditions that the liquid and residual vapour remain in contact, the vapour becomes progressively richer in the more volatile component until finally a composition C_{VS} is reached where all the vapour is condensed. The limit of enrichment C_{VS} is the composition of the vapour in equilibrium with a liquid having the same composition as the original vapour C''_{VS} and the amount of the enriched vapour is infinitesimal. If, however, the temperature of the condensing medium is maintained at a temperature t_2 so that when the original temperature t_1 of the vapour has fallen to t_2, there remain vapour and liquid also at t_2, and if the condensate weighs L'_S with a composition C'_{LS} and the vapour weighs V with a composition C''_{VS}, then,

$$\frac{\text{Weight of liquid}}{\text{Weight of vapour}} = \frac{C''_{VS} - C_{LS}}{C_{LS} - C'_{LS}} = \frac{L'_S}{V} \quad . \quad . \quad (48)$$

Simple Condensation.—If, however, the vapour is condensed under such conditions that the condensate is removed as fast as it is formed so that a succession of instantaneous equilibria is established, the vapour grows progressively richer in the more volatile component as above, but as the last of the vapour is condensed, its composition will have reached that of the pure component. Such a method of distillation is truly differential and can be called, and is often known as, differential condensation. As has been shown, the enrichment of the vapour can be calculated by means of the equation

$$\operatorname{Log}_e \frac{V'_S}{V_S} = \int_C^{C'} \frac{dC}{C_{VS} - C_L} \quad . \quad . \quad . \quad (49)$$

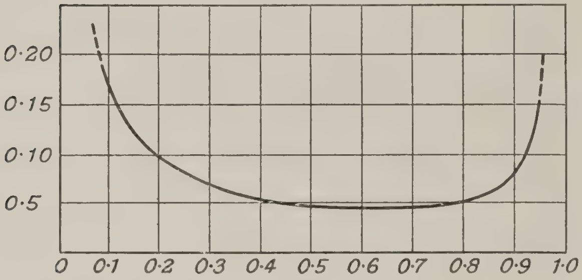


Fig. 14.—$\frac{1}{C_V - C_L} \sim C_V$ Curve. Benzene-Toluene.

and subsequent calculations. This equation can be solved graphically by drawing the $\frac{1}{C_{VS} - C_L} \sim C_{VS}$ curve similar to that shown in Fig. 14 or Fig. 2. The type of condenser in which this differential condensation is effected is termed a differential condenser.

Considering the two methods of fractional condensation, it is clear that as regards separation better results can be obtained with the second than with the first. Without forgetting that true and complete equilibrium are not attained under works conditions, equilibrium condensation can be approximately realised in practice.

Differential condensation involving the removal of each increment of condensate from contact with the residual vapour as fast as it is formed cannot be so easily accomplished, but it can be closely imitated.

Since separation by means of fractional condensation is obtained in some industries, more particularly in the petroleum refineries, while in others the same result is obtained by fractional distillation in column apparatus, it is desirable to effect a comparison. It might, however, be added that on the oil-fields it is desired to separate mixtures into fractions with different boiling-point ranges, while in most of the other distillation works actual separation of the pure components is usually the main object.

Fractionation Efficiency.[1]—Efficiency of separation should be compared by calculating the heat required to produce unit weight of distillate of a given composition, but as data regarding specific and latent heats are very limited it is only possible to work on a basis of the weight of liquid vaporised to give unit weight of product of a chosen composition.

Consider a mixture of equal weights of benzene and toluene with its equilibrium vapour 0·716 benzene. Consider three cases :—

1. Change in vapour composition from 0·716 to 0·816.
2. Change in vapour composition from 0·716 to 0·950.
3. Change in vapour composition from 0·716 to 1·000.

The minimum vaporisation for the three methods of separation were calculated by means of equations (48), (49) and (4) respectively, and the results are given in Table VI (see next page.)

If the efficiency of the ideal column is taken at 100 per cent., the efficiencies of the simple equilibrium condenser and the differential condenser are 65·7 per cent.

---

[1] Leslie, *Motor Fuels*, 1923.

TABLE VI

Minimum Vaporisation needed to Separate Unit Weight of Product

Change in vapour composition.		Weight of vapour necessarily formed in still in order to separate unit weight of product.		
From.	To.	Perfect simple condenser.[1]	Perfect differential condenser.	Ideal column.
0·716	0·816	2·22	1·684	1·46
0·716	0·950	Separation impossible.	4·792	2·08
0·716	1·000	Separation impossible.	Zero quantity of product can be formed.	2·32

and 88·7 per cent. respectively in case (1), and 0 per cent. and 43·5 per cent. in case (2). In case (3) separation can only be made in a column. These data show the superiority of fractional distillation over either of the two methods of condensation and also demonstrate that the second method is preferable to the first described, although this is evident, as already remarked.

Reflux Condensation.—Bearing these arguments in mind, attention can now be given to the condenser which is placed above the distillation column, and which condenses part of the vapour to form the reflux on to the top plate or section and therefore to the whole column. It was thought at one time that this condenser could be employed to give a useful fractionating action and that it would in this way assist the column in effecting an easier separation. With this object in view, various obstructions were placed in the tubes so that the liquid and vapour were intermingled. In such " mixed " condensers the vapour entered the bottom of the condenser and the liquid formed by condensation descended contra-flow to it. Each tube therefore became a small fractionating column, and the combined vapours from these minute columns passed to the final condenser in a supposedly much-enriched condition. Many inventors endeavoured to bring about improvements in condenser design to enable efficient fractionation to be obtained. It has been shown repeatedly by many writers that the fractionation obtained is usually insignificant and that the desired effect can be obtained with greater effect and efficiency in the column itself. It has already been shown that fractional distillation is more efficient than fractional condensation.

---

[1] Condensing under equilibrium conditions.

In the type of partial condenser usually employed nowadays, which consists of vertical tubes in a suitable body, the vapour enters at the top. The condensate formed runs down the tubes adhering to their surface in its downward course, while the vapour passes in an inner core between the surfaces and not in intimate contact with the condensate. Any possible fractionation is therefore very much less than in the mixed condensers described in the previous paragraph. As before, the enrichment is insignificant, and it is only in the column that economical fractionation can be obtained. Reference can also be made to the boiling point–composition curves such as Fig. 8 or Fig. 13, from which it will be observed that the largest differences in composition are effected in the lower plates of the column. The higher in the column we get, the smaller is the difference between the composition of the liquid on one plate and that on the one above. Unless the column is designed with an inadequate number of plates for the separation of the liquid mixture in question, the vapour from the top plate will be only slightly richer than the liquid from which it has arisen. The weak fractionating action of the condenser will not therefore be of much avail, and it is preferable to allow the column to do the work. The partial condensers in common use, constructed as they are with cooling surfaces only, have practically no rectifying effect, the composition of the condensate being practically the same as that of the original vapours.

The second of the two condensers usually used in modern stills was originally intended to condense the residual vapour from the partial condenser, which was assumed to act as a fractionating device. Although, as demonstrated, there is no appreciable rectification, or practically none, the two condensers are retained in the great majority of stills.

Complete Condensation.—Since in the majority of cases the composition of the condensate and the original vapours is almost identical in the reflux or partial condenser, the second or final condenser can be eliminated. In this case, the single condenser must be employed to condense all the vapours from the column, part of which forms the reflux, while the remainder constitutes the distillate proper. As, however, it is necessary that the reflux should be condensed only and not cooled below the boiling point before returning to the top plate of the column, it is necessary in most cases to provide a cooler to reduce the temperature of the distillate proper before it flows to the collecting box or receiver.

Advantages of a Single Condenser.—Although the elimination of the final condenser and the substitution for it of a cooler does not effect any great saving in the cost of the complete distillation apparatus, yet there are certain advantages which consist chiefly in greater control of the operation.

For any given column and any initial mixture composition there is a certain reflux ratio which gives optimum fractionation in the column. If the reflux is less than this, the distillate will not have the desired purity. If the reflux is greater a slight increase in purity may be attained, but the time and heat consumption for a given weight of product will be increased. In a discontinuous still, the composition of the charge and therefore of the vapour entering the column changes progressively with the distillation. In running any particular fraction it is necessary to increase the reflux ratio in order to meet this composition change. With the partial condenser the reflux is changed by altering the rate of flow of the cooling water, the exact effect of which can be predicted only by experience and determined only by trial, a great deal depending on the operator. Moreover, the full effect of a given change in the cooling water flow does not appear at once but develops slowly. Consequently, trial and error enter largely into the control, requiring close attention and frequent regulation in order to obtain satisfactory results.

In the case of the partial condenser, it is necessary to rely to a great extent on the judgment of the operator, and it is a difficult matter to issue instructions to him regarding best working conditions. In the case of a single condenser, the dividing box which receives the total condensate can be calibrated and provided with a scale to indicate the reflux ratio corresponding to any position of the divider. In this way, the reflux ratio can be adjusted to give a reasonable approximation to the optimum for the changing vapour composition.

In the case of the fractional distillation of liquids which boil at a higher temperature than water, the reflux is controlled in a partial condenser by partly filling the condenser with water, which is kept boiling by the heat absorbed from the vapour. The amount of reflux can be changed by altering the height of the water surrounding the condenser tubes, but exact regulation is difficult, since a slight increase in the height of the water may produce a large change in the condensate. With the single condenser, high-boiling liquids can usually be handled in the same way as low-boiling ones, the reflux ratio being easily controlled.

In the case of continuous stills where the partial condenser is used for preheating the crude liquor going to the column, complete condensation can be obtained as above by building the condenser in two parts, the upper section being the preheater, the lower completing the condensation of the vapours. The total condensate is then divided as before.

CHAPTER VI

HEAT TRANSFER

Heat may be transferred from one substance at a higher temperature to another at a lower temperature in one or more of three distinct ways :—

Radiation.—A hot body emits rays of heat (or light) which impinge on other cooler bodies raising the temperature of the latter in varying degree according to their capacity for absorbing heat.

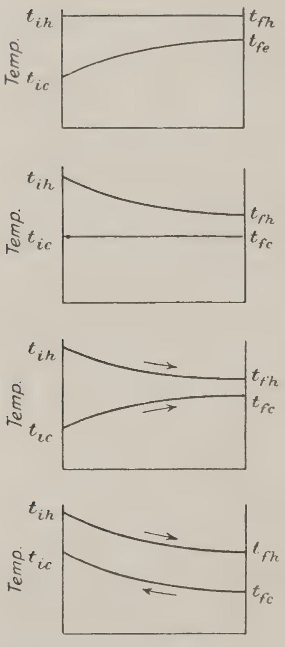
Convection.—This involves a movement of heated material from one point to another at a lower temperature so that heat is transferred. A hot water or steam "radiator" (so-called) transfers heat in this way, the heated air rising due to a difference in density caused by the heat and thus carrying warmth from the "radiator" to various parts of a room. Again, when a liquid is being heated up to its boiling point, the heat is transferred through the liquid mass by the convection currents set up.

Conduction.—In this process heat is transferred through a conducting material from one substance to another at a lower temperature but without appreciable displacement of the material particles.

All three of these processes are important when considering heat transfer in the case of boilers and fired stills where heating is accomplished by the combustion of a solid, liquid or gaseous fuel. For temperatures lower than 900 to 1000° F., such as appertain to heat exchange between gases or liquids in coolers, heaters and condensers, conduction and convection are of greater importance.

In the transfer of heat, the substances in question may be stationary or may be relatively in motion. The movement may be parallel or counter-current. The temperature of one body may remain constant while the other changes or the temperature of both may change. Four separate cases may be considered and are exemplified in Figs, 15, 16, 17, and 18. In all these

t_{ih} = initial temperature of the hotter substance.
t_{ic} = initial temperature of the cooler substance.
t_{fh} = final temperature of the hotter substance.
t_{fc} = final temperature of the cooler substance.



Figs. 15, 16, 17, 18.—Heat Transfer Processes.

Case I.—The hotter substance has the constant temperature t_{ih}, which equals t_{fh}. The cooler substance changes in temperature from t_{ic} to t_{fc} (Fig. 15). A typical example is that of heating a liquid up to its boiling point by means of steam at constant temperature.

Case II.—The cooler liquid has the constant temperature t_{ic}, which equals t_{fc}. The hotter substance changes in temperature from t_{ih} to t_{fh} (Fig. 16). A typical example is that of a steam boiler, where water is evaporated under constant temperature (or pressure) while the temperature of the flue gases drops in the passage through the boiler.

Case III.—Both substances change in temperature; they flow parallel to one another over the two surfaces of the dividing wall. The temperatures of the hotter and the cooler substances change from t_{ih} to t_{fh} and t_{ic} to t_{fc} respectively (Fig. 17).

Case IV.—Both substances change in temperature. They flow in opposite directions (counter-current) over the two surfaces of the dividing wall. The temperatures of the hotter and the cooler substances change from t_{ih} to t_{fh} and t_{ic} to t_{fc} respectively (Fig. 18).

Parallel and Opposite Flow.—Cases III and IV can be compared in a qualitative manner. In the case of parallel flow, Case III, the hotter liquid has its highest temperature at the beginning, while the cooler liquid has its lowest temperature. At the end, the reverse holds true. With opposite flow, Case IV, the hotter liquid and the cooler liquid have got their highest temperature at one end and their lowest at the other. Again, with parallel flow the cooler liquid must always run off at a temperature lower than the lowest temperature of the hotter liquid. But with opposite currents the cooler liquid may flow away at a temperature only slightly less than the highest temperature of the hotter liquid.

Further, with parallel currents the greatest temperature difference occurs between the highest temperature of the hot and the lowest temperature of the cold liquid. The smallest temperature difference occurs between the lowest temperature of the hot and the highest temperature of the cold liquid. The first difference is the greatest under any conditions, the second is always much less, which also holds for opposite flow. Since with opposite currents the highest possible temperature difference can never occur, it follows that in general the mean temperature difference is greater with parallel than with opposite flow, and consequently in the former case the necessary heating or cooling surface may be, nearly always, smaller than in the latter.

Opposite flow requires a larger apparatus, but uses less water for cooling or liquid for heating than parallel flow, and, in particular with similar materials, permits the attainment of the highest temperatures in heating apparatus and the lowest temperatures in cooling apparatus. It is impossible to obtain these with parallel currents. The important difference between the two methods of heating and cooling is not always appreciated by designers, and parallel flow is often seen where the alternative design should have been used. Only in certain particular cases is parallel flow advantageous, for example, where only part of the heat has to be removed from the hotter liquid, and where if less than a certain minimum temperature is attained the liquid to be cooled becomes too viscous to be handled.

Mean Temperature Difference.—Referring to the curves shown in Figs. 15 to 18, if these were straight lines the mean temperature difference would be the arithmetic mean of the initial and the final temperature differences. If, however, the transfer of heat is strictly proportional to the temperature difference, the curves are of the exponential type, except, of course, where the temperature is constant. The mean temperature difference is then given by the expression :—

Mean temp. diff.,

$$t_m = \frac{(\text{initial temp. diff.}) - (\text{final temp. diff.})}{\log_e \dfrac{(\text{initial temp. diff.})}{(\text{final temp. diff.})}}$$

$$= \frac{(t_{ih} - t_{ic}) - (t_{fh} - t_{fc})}{\log_e \left\{\dfrac{t_{ih} - t_{ic}}{t_{fh} - t_{fc}}\right\}}$$

$$= \frac{(t_{ih} - t_{ic}) - (t_{fh} - t_{fc})}{2{\cdot}3026 \log_{10} \left\{\dfrac{t_{ih} - t_{ic}}{t_{fh} - t_{fc}}\right\}}.$$

Coefficient of Heat Transmission.—The coefficient of heat transmission in British units is the figure expressing the number of British Thermal Units passing in one hour from a hotter to a colder substance through one square foot of dividing surface when the difference in temperature between the hotter and the cooler substance is 1° F. In metric units, the coefficient is expressed in calories transferred per hour per square metre per 1° C. difference in temperature. In the following, British units are employed, although the metric units are more convenient in many respects.

In the case where the hotter liquid or vapour is separated from the cooler liquid or vapour by a metallic wall, the coefficient of heat transmission, which we can designate by H, is made up of three coefficients as follows :—

R_1, Coefficient of heat transmission through the surface of the dividing wall.

R_2, Coefficient of heat transmission through the wall itself.

R_3, Coefficient of heat transmission through the opposite surface of the dividing wall to that considered for R_1.

Again, if we consider the flow of heat from (say) saturated steam to a liquid through a metallic wall, the main resistance "R" is the summation of three resistances as follows :—

r_1, a film of condensed steam on one face of the wall or plate;

r_2, the resistance of the metal plate;

r_3, a stationary film of water on the other face of the plate.

In addition to these resistances, there may be surface resistances due to corrosion.

In general, and as shown in Fig. 19, we may consider that on each side of a dividing metallic wall there exists a film moving with a velocity that varies from a value zero next the wall to the velocity of the main body of the fluid at some distance from the wall. Hence in order that heat may pass from one fluid or vapour to the other fluid or vapour, it must flow through the two fluid or gas films. Since most fluids and gases are very poor conductors of heat compared with solids, a great resistance to heat flow occurs at their boundary surfaces, so that a large temperature drop occurs at these places. If the conductivity of nitrogen and carbon dioxide is regarded as unity, that of paraffin base oil is 7, water is 26, wrought iron is 2900, and copper is about 19,500.

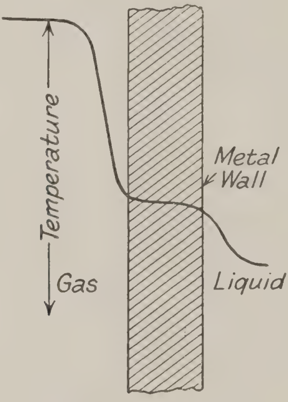


Fig. 19.—Temperature Drop.

It is clear that the temperature drop is chiefly due to the resistance of the two films and that the thermal resistance of the metal wall is only a small factor in the overall resistance. It has been shown by many experiments that the stationary film adhering to the face of the dividing wall becomes thinner as the velocity of the fluid increases and may become negligible at the highest velocities. In most cases, however, the temperature drop across the metal plate is practically negligible unless the metal is very thick or, as mentioned, the fluid flow is very rapid and therefore the films very attenuated.

It will be apparent that the thickness of the film is dependent on the viscosity of the fluid. Through this film heat can be transmitted by conduction only, but as soon as the heat has passed through the film, convection becomes possible, the hot molecules are absorbed by the main body of the liquid, and the resistance to heat flow becomes small. It is obviously advantageous to reduce this film effect to a minimum, and consequently turbulent flow is desirable.

The overall coefficient of heat transmission, H, equals the reciprocal of the total resistance to heat flow, R, and each component resistance equals the reciprocal of the component coefficient of heat transmission. That is,

$$H = \frac{1}{R} = \frac{1}{r_1 + r_2 + r_3} = \frac{1}{\frac{1}{h_1} + \frac{1}{h_2} + \frac{1}{h_3}}$$

whence $$\frac{1}{H} = \frac{1}{h_1} + \frac{1}{h_2} + \frac{1}{h_3}.$$

If it were possible to ascertain the value of the coefficient H or its components for each set of circumstances, the quantity of heat, Q, transmitted per hour could be easily calculated by means of the equation

$$Q = HAt_m,$$

where A is the area in square feet and t_m is the mean temperature difference which has already been discussed.

The coefficient H is, however, a complicated function of the velocity (or more probably of the mass velocity[1] of each fluid considered), the nature of the apparatus, the conductivity of the fluids and of the metal, and the condition of the heating surfaces. The present state of our knowledge concerning the value of H is such that it is rarely possible to make even approximately correct calculations. The only alternative is to determine the value for every individual apparatus and operation, which is essentially the method followed by most engineers.

Although a general law applicable to all cases may never be evolved, yet it is valuable to have some appreciation of the quantitative effect of as many of the variables as possible. To attempt any long review of the very considerable work carried out in connection with the determination of the individual factors is not only beyond the scope of this book and the limitations of available space, but such detailed references would be of doubtful practical value in the design of the necessary apparatus.

In the following, the discussion is for the most part qualitative and indicative of the general order of magnitude or of the particular nature of the individual problem. In the chapters dealing with distillation as applied to various industries empirical figures are given for heat transfer which have proved satisfactory.

Heat may be transferred either directly, as when steam is blown into a liquid, or indirectly, as in condensers, coolers, etc. In the latter case, the coefficient of heat transmission is made up of three component coefficients as already discussed. From the commercial point of view there are six important heat transmission processes which can be given in tabular form as follows :—

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[1] Mass velocity in British units is the number of lbs. of fluid per second per square foot of cross sectional area of the fluid path.

Heat transfer.	Examples.
1. Gas and liquid.	Some Scrubbers, Cooling Towers. Distillation and Absorption Towers.
2. Gas and solid.	Hot flue gases to solids in all types of furnaces. Recuperators, Regenerators, Economisers, Superheaters, Intercoolers, Brine Coolers.
3. Liquid and solid.	Heat Interchangers, Condensers, Coolers, Brine Coils.
4. Through metal wall.	In all indirect heating or cooling plant.
5. Condensing vapour and solid.	Condensers, Steam Coils, Partial Condensers.
6. Solid and boiling liquid.	Stills, Tube Stills, Boilers, Evaporators.

These can be briefly considered as follows :—

Gas and Liquid.—The direct transfer of heat from gases to liquids or *vice versa* has received very little attention, but reference can be made to a paper by Whitman and Keats.[1]

Gas and Solid.—This problem has received very considerable attention from many investigators. A typical equation is that of Nusselt [2] who passed air, at various pressures up to 214 lb. per square inch gauge, through a brass tube 0·87 in. i.d. and 1·02 in. o.d., the tube being surrounded by a steam jacket kept at 215° F. In its simplified form this equation is

$$h = b\left(\frac{W}{A}\right)0{\cdot}786,$$

in which W is pounds of gas per second and A the area of the gas path in square feet and

$$\begin{aligned} b &= 0{\cdot}00114 \text{ for air} \\ &= 0{\cdot}00094 \text{ for } CO_2 \\ &= 0{\cdot}00213 \text{ for steam} \\ &= 0{\cdot}00306 \text{ for coal gas.} \end{aligned}$$

The results of Nusselt are in fairly good agreement with those of Ser,[3] Josse,[4] Royds and Campbell,[5] Royds,[6] and Brabbée,[7] but not with those of Nicholson,[8] Jordan,[9] Kreisinger and Ray,[10] or Lewis, McAdams and Frost.[11] The equation of Weber may also be noted in which

$$h = \frac{4 \cdot 3 w^{0 \cdot 76} C p S^{0 \cdot 2} T^{0 \cdot 5}}{(\text{Mol. wt.})^{0 \cdot 3}},$$

where w = lb. per square foot sectional area.
C_p = the specific heat as constant pressure.
S = the reciprocal of the hydraulic mean depth in feet (in circular pipes $S = 48/d$ where d is the diameter of the pipe in inches).
T = absolute temperature °F.

The thermal conductivity of gases increases with the temperature, and consequently h is greater the higher the film temperature. On the other hand, the viscosity of gases, unlike that of liquids, also increases with increasing temperature, so that the two effects tend to neutralise each other. The result then is that, for the same temperature drop between gas and solid, an increased temperature range has little effect on the coefficient h. Thus the value of the coefficient for air at 750° F. is roughly double that at 60° F., but its viscosity is more than double.

Solid and Liquid.—A number of formulæ have been proposed by various investigators for the transfer of heat between a solid and a liquid or *vice versa*, but our knowledge is still very limited and inadequate. In this connection reference can be made to papers by Stanton,[12] Clement and Garland,[13] Webster,[14] Porter,[15] Richter[16] and Lewis, McAdams and Frost.[17] A close review of these and some other works does not reveal any marked degree of accordance, and all the results must be viewed with caution until more extensive and intensive experiments have been carried out and verified in practice.

Transfer through Metal Wall.—This is generally negligible unless the film resistances are very small, as in high velocity heaters. The relative conductivity of various substances is important and a few comparative figures are given in Table VII :—

TABLE VII

Relative Heat Conductivity

Copper	1000·0
Iron	160·0
Silica	2·5
Water (not in motion) . . .	1·4
Air	0·056

Gas–Solid–Liquid.—Considering the overall coefficient H in the case of heat transfer from a hot gas through a metal wall to a liquid, we have to consider the three component coefficients. Although our knowledge of these components is scanty and very unsatisfactory, it can be said that the main resistance to heat flow is that of the gas film, so that there is every reason for increasing the speed in order to decrease this resistance. Lucke [18] has shown that in the case of gas with a high and water with its relatively low thermal resistance, the velocity of the water in the tubes employed had little effect on H. Thus in the case of a plain tube and with the gas at 1000° F., the B.Th.U. per hour per square foot per 1° F. remained constant for water velocities between 5 and 85 ft. per minute. On the other hand, changes in the nature of the heating surface on the gas side and changes in the gas temperature were found to have pronounced effects.

When the resistance of the two fluids is comparable, H will be increased by increasing the velocity of both fluids. Otherwise there is little or no gain in increasing the water velocity, although increased turbulence is valuable.

Condensing Vapour and Solid.—Heat transfer in apparatus for the condensation of vapours, and more particularly for the condensation of steam, has been the subject of many investigations. The problem is a complicated one because vapours contain varying amounts of non-condensable gases, and further because the thickness of the film of liquid formed is variable. The thickness of the liquid film is determined, not only by the inherent properties of the liquid and by the conditions, but also by the nature of the apparatus. If the tubes are vertical the thickness of the liquid film increases from the top to the bottom of the tube. Obviously the rate of heat transfer through horizontal and vertical pipes will be very different.

McAdams and Frost [19] state that the film coefficient of heat transfer from condensing vapour to a metal surface is given by the expression

$$h = b \,.\, c \,.\, k \,.\, f \,.\, v^{n} \,.\, /m^{p}.$$

where b = experimentally determined coefficient of proportionality.

c = a cleanliness coefficient.

k = thermal conductivity of the condensate on the wall.

f = fluidity = 1/viscosity.

v = vapour velocity.

n = an exponent of velocity experimentally determined.

m = hydraulic radius of vapour passage.

p = exponent of m to be experimentally determined.

The original paper should be consulted, but the expression is interesting as showing the complexity of the problem. Their apparatus consisted of a 1½-inch pipe through which a brass pipe 0·675 inch o.d. and 0·49 inch i.d. passed concentrically. The vapour condensed in the annular space between the pipes and water flowed through the brass pipe in the same direction as the steam in the jacket. The values of h for the condensation of steam varied between 2010 and 2650 B.Th.U. per hour per square foot per 1° F. The average was 2400. These results are comparable with those of Clement and Garland,[13] who found values of 1470 and 2410 in a somewhat similar apparatus. For benzene and carbon tetrachloride, values of the film coefficient were found by McAdams and Frost, 340 and 280 respectively. It is interesting to note that if the coefficients for steam, CCl_4 and C_6H_6, are divided by the thermal conductivity and by the fluidity of the respective liquids the values obtained are 2240, 2500 and 1500 respectively. (Fluidity is the reciprocal of viscosity.)

Lewis, McAdams and Frost[20] give a tentative equation for the coefficient of heat transfer from a condensing vapour to a metal surface

$$h = 2200 \frac{k}{z}$$

where k = absolute thermal conductivity of the fluid.
z = viscosity of the fluid.

The effect of air on steam has been reviewed by C. S. Robinson,[21] who selects 3000 B.Th.U. per hour per square foot per 1° F. as a mean value for the film coefficient, but it is very difficult to measure the amount of air present, and in practice this air is not evenly distributed.

Webster[22] investigated the condensation of steam in an apparatus consisting of a $\frac{7}{8}$-inch o.d. and $\frac{1}{2}$-inch i.d. horizontally placed copper pipe jacketed concentrically with another tube $1\frac{3}{4}$ inches i.d. The steam condensed in the annular space and the cooling water flowed through the inner tube. Increasing the steam velocity from 1000 to 4000 feet per minute, when all the other conditions were constant, increased the rate of heat transfer from 1600 to 2400 B.Th.U. per square foot per minute per 1° F. Similarly, increasing the density of the steam from 0·05 to 0·20 lb. per cubic foot by increasing the pressure while other factors remained constant increased the rate of heat transfer from 1600 to 2100 B.Th.U.

Solid and Boiling Liquid.—This also is a complicated problem and very little work has been done in connection therewith. Reference can be made to four very valuable papers by Badger[23] in connection with evaporator design in which the effect of temperature difference, of temperature at which heat transmission occurs and of hydrostatic head has been studied.

Overall Coefficient of Heat Transfer.—The foregoing discussion of the component factors of the overall coefficient of heat transmission is of necessity in the nature of a sketch, but may serve to indicate the great complexity of the problem and also to give various references which can be consulted for further information. There is no general law or formula which can be used in the accurate design of heating and cooling surfaces, and it is quite probable that there never will be a really satisfactory one. Although the film conception is very instructive, yet, in the present state of our knowledge, it may tend to bring confusion rather than actual help. In the practical design of apparatus it is the overall coefficient that the designer uses, and for the greater part he relies on previous experience. Until the individual resistances to heat flow are analysed, the more or less empirical rules will remain, but it would be decidedly advantageous to understand at least the elementary principles of heat flow. Yet again and again one finds an utter lack of appreciation of fundamentals.

On the other hand, every design involves a factor of safety to allow for abnormal conditions, and this very often covers a multitude of evils. In the author's experience in the design of large distillation plant, there is no necessity to strive after extreme, almost scientific, accuracy, but it is surely worth while to understand in a quantitative way as many of the variables as possible. The fewer the factors that are imperfectly understood the closer the guess as to their effect and the necessary allowance therefor. Scattered about in the literature on heat transmission will be found particles of useful and authentic data which, *plus* a reasonable ability to draw analogies, *plus* experience and *plus* some common sense, will enable a satisfactory design to be evolved which will *work* when converted into the necessary plant.

As an example of lack of appreciation of principles, there can be instanced the frequent use of superheated steam supplied to heaters with the object of increasing the duty. When steam is thus superheated it becomes a gas, and the resistance of the gas film is much greater than that of a liquid film. As a result, the transmission of heat is retarded instead of accelerated. In addition, if the steam is superheated because its temperature in the saturated state is less than the boiling point of a liquid which has to be distilled, no condensation can occur until the superheat is all removed. But the steam temperature is then less than that of the liquid and therefore it cannot be condensed, so that the latent heat cannot be extracted. The net result is that the rate of heat transmission falls and the steam consumption for a given duty becomes enormous.

In general, the recognised method of reducing the film resistances to heat transfer is to increase the velocity, or, more properly, the mass velocity of the fluids. In all cases, the velocity of the fluid should be greater than the greatest critical velocity, for if the average velocity is less than the critical, the velocity at the surfaces of the metal wall separating the fluids is zero.

When the fluids move at greater rates than the critical velocity, the flow is turbulent and the thickness of the stagnant or slow-moving fluid film next the metal is reduced with a consequent increase in the heat transfer. The greater the velocity the better, in so far as heat transfer is concerned. The relationship between mass velocity and rate of heat transfer is not lineal, for, as shown in Nusselt's equation, for example, the quantity $\left(\frac{W}{A}\right)$ has an exponent 0·786.

Economy of operation limits the velocity, because as the velocity increases the pressure required to force the fluid through the apparatus also increases.

Another factor entering into design is the mean distance of all the particles of the fluid from the heat-transferring surface. This is allowed for in mathematical expressions by introducing the hydraulic radius. The ordinary coil condenser in a tank is convenient, but inefficient because the water moves sluggishly and the mean distance of the particles from the coil is great. Also there is practically no chance of turbulent flow such as occurs when water flows in a pipe above the critical velocity.

The foregoing discussion, although incomplete, will probably be sufficient to indicate how complex is the study of heat transfer, and how far we are at present from the evolution of a general law. It is probable that the average designer will continue to use his specialised but empirical knowledge accumulated in practice in preference to struggling with film coefficients and laws the accuracy of which is not above suspicion. But there should always be a reasonably intelligent appreciation of the influence that the various components have on the overall coefficient. In the next chapters the subject is touched on again in connection with certain parts of plant used in distillation.

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CHAPTER VII

DISTILLATION APPARATUS

Stills and Columns

The type of distillation apparatus used in any particular case depends on a number of circumstances such as the object of the distillation, the nature of the original mixture, the method of heating employed, and so on. Each distinct branch of distillation has evolved apparatus which more or less suits the particular conditions involved, and in some industries a certain type or design has become almost standardised. It does not necessarily follow, however, that an accepted piece of plant is the most suitable and economical form that could be used, for there are several instances where it would appear that equally effective and even more efficient work could be done by other plant at a reduced cost. Custom and familiarity with the use of a particular type have largely determined the survival of certain processes, and those responsible are perhaps timid about venturing on paths along which others in the same business have not passed.

In the following discussion the various components of complete distillation plants are briefly described and certain comments made regarding them, although limitations of space preclude any detailed examination. Many of the points raised should be mere commonplaces, but it is strange how often the elementary fundamentals are ignored either through lack of knowledge or indifference.

Fired Stills.—The simplest distillation apparatus consists of a closed vessel or still heated by direct fire and provided with an outlet leading the vapours to some form of condenser. The burning of any fuel necessarily involves high temperatures, a fact which, coupled with the nature of the charge, has a considerable influence on the design of the still, the method of working and the material of which the plant is constructed.

Vertical Stills.—In the case of the ordinary vertical tar still (Fig. 40, p. 174), which can be regarded as the standard type in the coal-tar industry, not only does the usual concave bottom possess greater inherent strength and larger heating surface than a flat one, but it allows for contraction and expansion without unnecessary strain and also enables the run-off pipe to be at the lowest point at the side of the still, and therefore out of contact with the flame.

The drawback to the concave bottom is the difficulty in cleaning out the still efficiently, for there is a tendency for the pitch left in the still to lodge in corners and ultimately to coke. This trouble is overcome for the greater part by using a channel plate instead of an angle to connect the bottom to the still, but care in cleaning is still needed. On the other hand, with a convex bottom, although cleaning is greatly facilitated and although there is the same increased heating surface over a flat plate and the same provision for contraction and expansion as in the concave form, yet the run-off pipe for the pitch must be connected to the centre of the bottom, so that both the joint and much of the pipe are subjected to the greatest heat.

Some users prefer to protect the rivet heads and bottom with a fire-brick curtain, which is only possible with the concave form. Again, the number of rivet heads can be greatly reduced by making the still bottom in one piece, but this is not considered good practice by many distillers because the repairs are more costly. In any case, a solid bottom is limited to the smaller stills.

The material for a tar still is usually wrought iron or mild steel. From the point of view of corrosion, cast iron would be excellent, but it makes a heavy still, and since only the convex bottom can, for practical reasons, be made and used, the run-off pipe is at the centre and therefore in the zone of greatest heat. In general, the use of cast iron for distillation work involving fire heat and high temperatures is of doubtful advantage, for the comparatively poor expansive properties and low tensile strength of the metal render it peculiarly liable to crack. In the case of a bottom run-off, the danger of cracking is accentuated on account of the greater thickness of metal which occurs at the junction of this pipe to the bottom. Great care is necessary to ensure that a cast-iron vessel which has been fire-heated is allowed to cool slowly, and the design should be carefully made with every respect for the inherent weakness of the material.

On the other hand, fire-heated cast-iron "cracking" stills with hemispherical bottoms are used in the Russian oil-fields, but these have no bottom outlets, the residual coke being removed from above. Also cast-iron stills with bottom outlets are successfully used in the distillation of fatty acids, the final still temperature being 570 to 600° F. Nevertheless, the attractiveness of cast iron in many respects must not be allowed to cloak its weakness in the direction indicated.

Horizontal Stills.—In the petroleum industry, fire-heated stills of the horizontal form have been adopted in which the fire is underneath at one end, the gases passing along the bottom and dropping down at the far end into a flue which usually serves for a number of stills side by side. As far as possible, the rivet heads and caulking edges are kept away from the heat. Thus, as seen in Fig. 33, p. 154, of an 85-ton still, the bottom is composed of two plates, $\frac{1}{2}$ inch thick and 18 feet long, the longitudinal rivets being away from the centre line, while there are only three latitudinal seams. Smaller plates are used for the sides and top, since the fire does not reach them. For coking stills, the bottom is $\frac{5}{8}$ inch and over.

When these stills are worked on the batch principle, the area of bottom exposed to the heat is usually reduced to about one-third of the circumference, to avoid exposure of a portion of the bottom to the gases when there is no oil on the other side to conduct away the heat. With continuous working and a constant oil level in the still, the area exposed to heat may extend to half the circumference, with consequent increased evaporation.

Compared with the vertical stills mentioned above, the chief disadvantage of the horizontal type is the increased fuel consumption, for the gases pass along the bottom only, whereas in the vertical type they pass into one or two openings leading into flues which circle above and around the annular brick ring (on which the still rests) to a suitable height up the sides of the still. On the other hand, whereas the average tar still is of 15 to 20 tons capacity, the smallest horizontal still in the petroleum industry holds 25 tons and the largest 170 tons and over. Vertical tar stills of 50 tons capacity are probably the largest made. With larger sizes, there is difficulty with the even distribution of heat, and very high shells are out of the question. Crude petroleum stills are sometimes made with internal flues like a Lancashire boiler, but the simpler outside-fired type is generally preferred.

Pipe Stills.—The modern pipe still consists of a continuous coil of pipe set in a chamber and heated by fire. The mixture is pumped through this pipe and is discharged in a heated condition from the coil into a large chamber called the separator, from which the vapours evolved are led to condensers of various types. This form of still is used in the coal-tar industry to some extent, but principally in connection with petroleum, since in the latter case continuity of supply is more or less assured, whereas the tar distiller cannot estimate the quantity of tar that he may expect to obtain from the various gas works, as their make is a seasonal one and dependent on climatic conditions. The comparative merits of continuous and discontinuous distillation methods have already been discussed.

Direct heating by fire is also employed for distillation purposes in other industries and for many individual processes, but the above examples are typical of the types of plant used. The shell stills mentioned above can also be worked continuously as described in Chapters X and XI, the horizontal type being usually employed.

Methods of Firing.—The method of firing depends on local circumstances, but in probably the majority of cases solid combustible, coal, coke, anthracite, etc., can be burnt. The weight of fuel per square foot of grate area, the useful heat available therefrom, the temperature of the fire, etc., are very variable, depending on the requirements of the distillation, the skill of the fireman and the grade of fuel used. A very common fault is the provision of too small a combustion space by placing the stills too close to the grate. This results in the gases striking the relatively cool still bottom prior to complete combustion, with consequent poor efficiency and smoke. Oil can be used when plentiful, but it is too expensive in this country for most purposes. Residual fuels, pitch, etc., have been used. For large works producer gas firing has the advantage that the distillation can be controlled somewhat more easily and less labour is needed to work a battery of stills. If the installation is large enough, the extra coal burnt in the production of gas is compensated by the saving in labour, although in the case of a row or battery of discontinuous tar stills run in proper rotation the labour and expense are not very high.

Steam-heated Stills.—Steam as a heating medium for distillation purposes can be used indirectly, as in steam coils immersed in the liquid charge, or directly as when it is blown into the mixture. Indirect heating will be considered, and in this connection reference can be made to the chapters on fractionation, so that the following may be regarded as a sequence to the matter discussed therein.

Size of Still.—The size of a discontinuous still is mainly determined by the quantity of liquid to be distilled in a given time per day or week. The distillation may be more or less independent of other operations, or it may be so intimately connected with some cyclic process that it is essential for the operation to be performed systematically.

If there is a regular daily supply, distillation may also be daily, or if the quantities are sufficient a larger still may be used and the distillation spread over two or more days. A larger still has the advantage that if a fractionating column is involved, the size of intermediate fractions to be redistilled does not increase proportionately to the quantity handled, radiation losses are less, there is a saving in capital cost over two stills of half the distillation capacity, and the labour of cleaning, filling, etc., is reduced. On the other hand, unless there is an assured regular supply, too large a still may become an absurdity, an event for which trade conditions are usually responsible.

In cyclic processes the size of still is, of course, determined by the output of the main product in the plant of which the still is a component part. It may be necessary to work such a still daily, or it may be possible to distil periodically by collecting sufficient liquor to form a reasonable still charge.

The size of a still is also determined by the liability for the charge to foam or froth. If there is no danger of such entrainment the charge may occupy up to 75 per cent. of the full capacity, provided the distillation is started very gently, but 70 per cent. is preferable and

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65 per cent. on the safe side. For liquids which froth badly, the charge may occupy only 50 per cent. or less of the full capacity.

Having decided on the still capacity, the actual dimensions offer no difficulty. Occasionally the space available must be considered, but otherwise all stills should be made as standard as possible, so that the coils may be interchangeable and spares reduced to a minimum. The design of rivets and other details need not be considered here, but one important point is to make sure that the joints are caulked on both the inside and outside. This is not infrequently omitted or forgotten by the maker.

Types of Steam Coils.—The steam may be used in coils, *i.e.*, long pipes with an inlet for steam and an outlet for hot water; or cast-iron steam chests may be bolted to each end of the still and connected by tubes expanded into the end plates of the still or the steam chests themselves. Coils are suitable for most stills, and are advantageous when the residue in the still is such that cleaning is necessary after running off. Coils are easily removed and put back again, whereas tubes are expanded and cannot be removed. Tubes are only suitable for short stills, and if one leaks both steam chest covers must be removed in order to renew or plug it up temporarily. In such a case distillation must be stopped, whereas a damaged coil can be shut off and the still worked on the others, which should always be possible if the designer has allowed sufficient heating surface.

Steam Pressure.—The steam pressure in a coil must be sufficiently high to boil the mixture at all stages of the distillation, so that the available pressure must be such that the steam temperature is greater than the highest boiling point. The temperature difference required depends on the liquid being distilled, but for many purposes can be taken as at least 40 or 50° F. The pressure in the coils and therefore the temperature are, of course, controlled by the valves.

Heating Surface.—The heating surface depends naturally on the amount of evaporation per hour. In the case of straight distillation, if the latent heats of the main components of the mixture are known and also the rate of distillation in, say, gallons per hour, the heat units needed per hour are easily calculated. In the absence of such data it is necessary to refer to other similar distillations for the approximate information desired and to err on the right side.

If a fractionating column is used, then the re-evaporation of the reflux must be considered. The exact value of the reflux ratio varies with the number of plates in a plate column or the height of a packed column, the ease with which separation of the liquid components can be effected and the amount of the intermediate fractions. The coils must, of course, be capable of distilling that fraction which requires the most heat units, and if the reflux ratio is known and also the latent heats, the amount of heat needed can be estimated. For simple mixtures, the methods developed in Chapters III and IV are useful, but it is doubtful if many works would adopt such. For complicated mixtures the heat requirements can only be ascertained by experience and judgment. During any distillation the composition of the charge in the still is continually changing and therefore the conditions in the column are also changing. If the composition of the distillate remains constant, the reflux ratio must constantly increase. If the rate of evaporation remain constant, the rate of distillation will decrease (since the reflux ratio increases).

To obtain a correct estimate of the value of these changes is a matter of considerable difficulty, but most designers are conversant with similar stills or have records which enable them to make the necessary allowances. There is no necessity for extreme accuracy, for a factor of safety covers much. If the maximum heat requirements have been even roughly ascertained an allowance of 50 per cent. extra surface will be satisfactory for clean mixtures. In the case of dirty liquids which cause incrustations or lodge dirt on the tubes, 100 per cent. extra heating surface may be necessary. No simple rules or law will cover all cases, but the more or less empirical rules or accumulated observations may be supplemented and qualified by an acquaintance with the fundamental principles of heat transfer. If there is to be a guess it might as well be a reasonably close one.

If an estimate of the maximum heat requirements can be formed, the necessary heating surface can be ascertained with sufficient accuracy for all practical purposes. In this connection, Table VIII can be consulted, which is that given by Hausbrand, but altered to read in British units as far as the coefficient of heat transmission is concerned.

Table VIII

Coefficient of heat transmission in British Thermal Units per square foot, per 1° F. per hour between steam and boiling water for copper coils 10–150 *mm. bore and* 1–30 *m. long.*

	Length of tube in metres.								
Bore of tube in mm.	1.	2.	4.	6.	8.	10.	15.	20.	30.
	Coefficient, H.								
10	3800	2694	1900	1543	1346	1202	982	858	714
15	3116	2200	1543	1266	1099	982	790	682	567
20	2694	1900	1346	1198	950	844	682	601	491
25	2400	1704	1202	982	850	760	620	537	438
30	2200	1543	1098	902	775	682	567	491	401
35	2038	1454	980	780	700	640	528	454	370
40	1900	1346	950	775	673	601	491	422	349
45	1790	1267	902	720	633	567	460	401	322
50	1704	1202	851	682	601	537	438	380	311
60	1542	1098	775	634	548	491	401	349	283
70	1440	1016	720	586	508	454	378	322	262
80	1346	950	673	548	475	425	342	298	245
90	1266	902	634	516	449	401	322	282	231
100	1202	858	601	491	427	380	312	273	220
125	1143	760	537	438	364	340	278	240	196
150	982	682	491	401	348	311	253	220	181

To allow for incrustation and scale on the tubes, for air present in the liquid, etc., the coefficient, *H*, should only be taken at about two-thirds of the values in the table. Thus the values of the coefficient for various metals becomes

For	copper	tubes,	about	2	mm. thick	0·66	of values	in table.
,,	W.I.	,,	,,	3·5–4	,,	0·50	,,	,,
,,	C.I.	,,	,,	10	,,	0·33	,,	,,
,,	Lead	,,	,,	10	,,	0·30	,,	,,

A table like this is useful for giving reasonable data on which to base the ultimate heating surface, but, in addition, it demonstrates the effect of bore and length on the heat transmission. It will be seen that the coefficient for a given diameter of tube is less the greater the length, due, of course, to the continually increasing amount of water from the condensation of the steam. It will also be seen that for coils of a given length the coefficient decreases with increasing diameter. The cross-sectional area increases as the square of the diameter, but the circumference as the diameter only, so that for a given volume of steam the velocity is greater in a small than in a large tube. This increased velocity not only increases the heat transmission by reducing the gas film as discussed in the previous chapter, but also prevents undue lodgment of the condensed steam, which is a bad heat conductor. The actual choice as regards the number, diameter and length of coils required in any given case is, of course, influenced by questions of design and construction, and it is not possible always to satisfy all the requirements.

Assuming that the maximum heat requirements are found to be 250,000 B.Th.U. per hour, including 10 per cent. radiation losses, then with a mean temperature difference of, say, 50° F. and a coefficient of heat transmission of, say, 500 B.Th.U. per square foot per 1° F. per hour, the heating surface would be

$$\frac{250{,}000}{500 \times 50} = 10 \text{ square feet,}$$

which constitutes the basis on which to design the coils. The factor of safety to be used depends on the liquid to be distilled. The possibility of fluctuations in the boiler pressure must always be remembered and can only be counteracted by a still further increase in the factor of safety. Of course, if the pressure falls so low that boiling ceases no extra heating surface will be of avail.

Fractionating Columns.—The theory underlying the use of a fractionating column has already been discussed. The function of this piece of apparatus is the separation of liquids of different volatility, and the ideal process consists in bringing upward-flowing vapour and downward-flowing liquid into such intimate contact that equilibrium is established between vapour and liquid at all points. The ascending vapour becomes richer and the descending liquid poorer in the more volatile component and, ideally, the change in composition takes place continuously and in truly differential manner. The working column can approach, but never equal, these ideal conditions, and it is the object of all column design to increase the intimacy of contact and therefore the efficiency of separation.

For the purposes of this book, three types of column will be considered: (1) Packed Column, (2) Perforated Plate Column, (3) Bubbler Hood or Bell Column. There are also "Full Columns" and "Sloping Columns" for alcoholic mashes and mechanical columns, but these will be omitted, since the other types are more common.

Packed Columns.—These columns consist of vertical cylindrical shells into which are inserted more or less promiscuously any material which will break up the vapour and liquid and so cause intimate contact between them. Any inert material may be used, as packing provided it is not attacked by the vapours. Quartz, porcelain, coke, iron, steel and other packings have been employed and have given fair results.

The requirements of an effective tower packing are that it should afford maximum surface per unit volume occupied, that it should give horizontal as well as vertical flow and mixing and that it should not retain excessive quantities of liquid. In distillation work the chief requirement of a packing is intimacy of contact between vapour and liquid.

With many packings there is a tendency towards channelling, the ascending vapour and descending liquid moving along the passage which offers the least resistance to their flow. This can be partly overcome by using a uniform material and putting it in place very carefully by hand. A great improvement on the older packings is given by the Raschig rings, which are called after the name of their inventor and consist of thin walled cylinders of equal length and diameter. They may be about 25 mm. diameter, about 55,000 of which occupy a cubic metre. Other sizes are made as desired, thus a 1 inch ring has done good work. Such a sized ring would give about 73 per cent. of free space, 58 square feet of surface per cubic foot, would weigh about 40 lb. per cubic foot, and about 1350 rings would occupy the same volume.

In general, packed columns are best employed in cases where the separation is comparatively easy, but for intensive fractionation they are not so suitable. Raschig rings and similar devices, such as those of Lessing, Goodwin, and Prym, can be more advantageously employed than the older and cruder types, but in the case of two Raschig ring columns used by the author on quite simple separations no great success was noticed.

On the other hand, packed columns are cheap to construct and have the advantage of offering little resistance to the vapour. In a fractionating column, however, resistance, and therefore pressure, is usually a minor point compared with the necessity for intimate contact between liquid and vapour. In connection with the resistance offered by different kinds of packing, reference can be made to an interesting paper by Zeisberg (*Chem. and Met. Eng.*, 1919, **21**, pp. 765–6).

Perforated Plate Columns.—A perforated plate column consists of a cylinder containing horizontal plates or partitions bored over the whole surface with small holes through which the ascending vapour bubbles into the liquid on each plate. The descending liquid flows down from plate to plate through suitable overflow pipes, the lower ends of which are sealed in a cup on the plate below. If the velocity of the vapours is such that no liquid flows through the small perforations good fractionation is possible, but if the speed is too high considerable entrainment is possible, while if too low the plates will empty. Such a column is not therefore very flexible, since the vapour velocity must be maintained constant or at any rate within certain limits which are fixed by the size and number of the perforations. Nevertheless, the perforated plate column is preferred to the bell type by at least one well-known firm of plant builders, and is reported to give excellent results, *e.g.*, in connection with both the primary and final distillation of crude benzol.

Bell Columns.—The bell column is accepted by most distillers as the most efficient fractionating device, especially for difficult separations. Fig. 20 shows a sectional diagram of such a column, in which it will be seen that the horizontal plate, *A*, is provided with a number of vapour pipes, *B*. The vapour rising up the column passes through these pipes, but is forced downwards by the bells, *C*, provided with serrated or slotted edges which are immersed in the liquid on the plate. These serrations or slots have the effect of dividing the vapour up into a number of streams, so that a scrubbing action is obtained between the liquid and the vapour. The depth of the liquid on the plate is regulated by the height of the overflow pipe, *D*, down which the liquid flows but up which the vapour cannot ascend, since the downpipe is sealed in the liquid on the plate below. Similarly, liquid cannot descend by the vapour pipes, since the tops of these are higher than the level of the liquid.

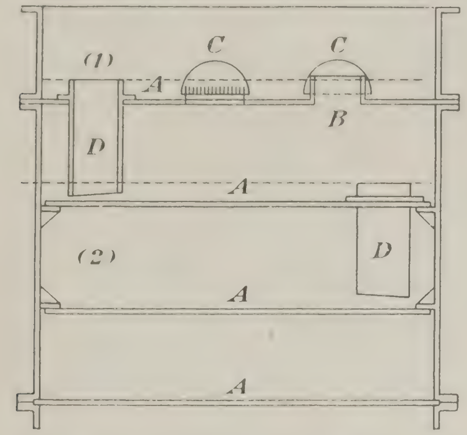

FIG. 20.—Section of Column.

A bell column may be constructed of any metal which will not be attacked by the liquids being distilled, but it is always desirable to reduce the number of external joints to a minimum. A column of cast-iron rings with a plate between each as shown by (1) in Fig. 20 is the worst in this respect, since there are two joints for every plate in the column. Type (2) shows a better design involving one joint for every three plates. As will be seen, two plates are carried inside the ring by annular shelves. The third plate rests in recesses in the top and bottom flanges of two rings. If steel or some other ductile material is used, there may be three plates inside the steel ring, the centre one being fixed in position before the angle iron for carrying one of the others is riveted on. One joint only need be used between each steel ring if both the flanges and the plate are recessed. Size of column is, of course, a determining factor in connection with such details.

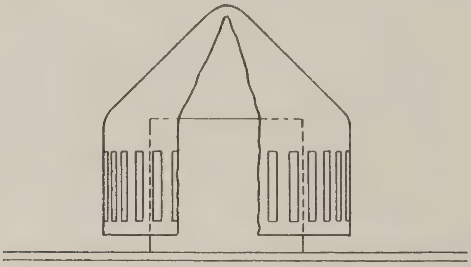

FIG. 21.—Bell for Thick Mashes.

Bells.—The bells and the vapour pipes that they cover vary in size and shape according to the liquids being distilled and whether the operation is continuous or intermittent. Thus in the case of continuous ammonia stills, the bells or hoods are large, since they have to be periodically removed for cleaning purposes, an operation for the carrying out of which suitable manholes are provided in the column shell. Continuous stills for the concentration of thick alcoholic mashes are also provided with bells of special design, of which Fig. 21 is an example. This bell is provided with a conical top, which is intended to prevent deposition of solid matter from the wash. In the case of discontinuous distillation, any solid matter in the liquid mixture is usually left in the still, and in the majority of cases the question of cleaning does not arise. In such cases the design of the bells is chiefly concerned with intimacy of contact between liquid and vapour.

The chief function of a bell is to increase the area of contact between the bubbles and vapour, and every effort should be made to ensure this in order that equilibrium may be approached as closely as possible. It has been established by the use of the cinematograph that the vapour leaving the slot of a bell does so in a series of bubbles and not, as would appear to the eye, in one continuous stream. These bubbles leave at a high speed varying from 10 to 15 feet per second, and although the movement is momentarily horizontal, it is quickly changed to the vertical. The bubbles rush to the surface and burst there. The interval of time is so small that only the exterior of the bubble can be affected.

The volume of a sphere is $\frac{4\pi r^3}{3}$, and the surface is $4\pi r^2$. If a spherical bubble of 4 mm. diameter is split up into eight smaller bubbles, these will have a diameter of 2 mm., but the surface exposed to the liquid will be doubled. This splitting and general deformation of the bubbles can be attained by bringing the bells sufficiently near other other so that actual collision occurs between the issuing streams of vapour.

Overflow Pipes.—The depth of the liquid on the plate and the "seal," *i.e.*, the height of the top of the liquid above the top of the bell slots, are determined by the height of the overflow pipes. Generally speaking, there is no need for a deep seal; it is more important that there should be maximum deformation of the bubbles.

For many purposes $\frac{5}{8}$ to 1 inch is ample, and much more than this only increases the back pressure without any marked improvement in the direction of equilibrium.

The position of the overflow pipes is important. With small diameter columns it is sufficient to put the overflow on one plate diametrically opposite to that on the plate below so that the liquid descends the column in a zigzag manner. With columns of a diameter greater than about 4 feet, two overflow pipes are advantageous placed symmetrically about either side of a diameter, the intention being that the part of the plate at right angles to the diameter at the centre should receive the same amount of liquid as the central portions, which are more favourably situated since they lie in the direct path of the flow. Retaining the single overflow pipe, the same object may be attained by means of guiding partitions which tend to direct the liquid to all parts in an evenly distributed manner. But the extension of this idea to the point of covering the whole plate between the bells with guiding partitions is, in the author's opinion, valueless and unnecessary. The greatest deformation of the bubbles can be attained by collision between them moving in opposite directions, but a bubble only hits a guiding partition with half this velocity.

Limitations of space preclude a more detailed analysis of the many purely practical points which require attention in the design of stills and columns, but some of the salient features have been mentioned. The distillation apparatus as a whole is briefly discussed at the conclusion of the next chapter.

CHAPTER VIII

DISTILLATION APPARATUS (*continued*)

CONDENSERS, COOLERS AND HEAT INTERCHANGERS

IN apparatus used for the purposes of condensing, cooling and heat interchange as applied in the majority of distillation processes, the two fluids are separated by a metal wall, and only this type will be considered here, since transfer of heat by actual mixing is not common. The very inadequate state of our knowledge concerning heat transfer has already been discussed in Chapter VI and mentioned in connection with steam coils in Chapter VII. In the design of condensers and coolers similar difficulties are experienced.

It will be remembered that the resistance of a gas film is much greater than that of a liquid film. Most vapours in distillation work contain appreciable amounts of uncondensible gases, the exact amount of which is usually unknown. Of these gases, air is that most frequently found; its presence in a liquid is, in fact, essential for boiling. Other gases are, of course, present in various mixtures, such as CO_2 in alcoholic mashes, but it is sufficient here to regard air and these gases simply as gas. In the same way, the liquid used—usually water—for condensing and cooling purposes frequently contains dissolved gases that are evolved when the liquid is heated and even dissolved solids that may vaporise. Consequently in a condenser there may be a gas film and also a liquid film on both sides of the dividing wall.

To reduce these film resistances to heat flow it is necessary to increase the velocity of the fluids until it is greater than the critical velocity, so that turbulent flow is caused. At less than the critical there will be a stagnant film of gas and liquid. Increase in the speed of the vapour to be condensed removes the adhering condensed vapour and reduces the gas film. Increase in the cooling water affects the transfer of heat in the same way. Whether it is possible or economical to obtain this increased velocity in any particular case is a matter to be considered, but the first sound principle to be remembered in condenser design is that the speed of both vapour and condensing medium should be greater than the critical velocity.

The comparison between parallel and counter-current flow has already been made, and it need only be repeated that counter-current flow is cheaper to work, gives a higher temperature if heating is the object and a lower temperature if cooling is desired, but requires a larger heating or cooling surface than parallel flow. In general, all condensing and most cooling apparatus should be constructed on the counter-current principle.

There are, of course, many other points to be considered in the design of condensers and coolers, such as simplicity and accessibility. The materials used in the construction should be suitable for both the vapours to be condensed and the liquid used as cooling medium. Provision should be made for the removal of gas if there are any unavoidable pockets in which this might collect. One important detail often forgotten is the provision of a run-off for the water in the condenser body when it is not working.

Condensing and Cooling Surfaces.—In the majority of cases where it is desired to convert a vapour into liquid by condensation, it is also necessary to consider the subsequent cooling of the condensed vapour to a reasonable temperature. The two operations of condensing and cooling are frequently carried out in the same, but sometimes in separate, pieces of plant. Assuming that the apparatus is built on the counter-current principle, the entering water has first to cool the condensed vapour and then to condense the vapour itself. It is necessary to consider these two stages separately, but it must be remarked that in approaching the question of designing a condenser there are often a number of conditions which are not known beforehand. Thus the temperature of the cooling water used may vary considerably, according to the season of the year, the average speed of the vapours entering the apparatus may be uncertain and many other factors have to be contemplated, the magnitude and effect of which are insufficiently known. In most cases it is necessary to make certain assumptions, and in all cases it is essential to allow for any departure from the assumed conditions by a reasonable factor of safety.

It must be clearly stated, however, that too much reliance must not be placed on calculations, for, as has been repeatedly stressed here, our knowledge of the values of the three coefficients which make up the overall coefficient is uncertain. In many cases estimations of the necessary heating or cooling surface are of great benefit, inasmuch as they enable the designer to ascertain the general order of magnitude so that very gross errors will not be committed. As an example of the general principle to be adopted, the following will perhaps be of interest.

Example.—Assume that 500 lb. of steam per hour at 212° F. have to be condensed and cooled to 80° F. with cooling water entering at 50° F. and leaving at 150° F. We have

Latent heat removed = 500 × 966 = 483,000
Sensible heat removed = 500 (212–80) = 66,000
Total heat removed 549,000

of which about 88 per cent. is latent and 12 per cent. sensible heat.

The cooling water is raised from 50° to 150° F., *i.e.*, through 100°, of which 12° is accounted for in the cooling period and 88° in the condensation operation. The temperature of the water at the point where condensation is complete and cooling starts is $50 + 12 = 62°$ F.

The mean temperature difference for the condensing period is calculated by the formula given on p. 80 and equals

$$\frac{(212 - 62) - (212 - 150)}{2{\cdot}3 \log_{10} \dfrac{212 - 62}{212 - 150}} = 100° \text{ F.}$$

The mean temperature difference for the cooling period is

$$\frac{(212 - 62) - (80 - 50)}{2{\cdot}3 \log_{10} \dfrac{(212 - 62)}{(80 - 50)}} = 75° \text{ F.}$$

The amount of water required is $\dfrac{549{,}000}{150 - 50} = 5490$ lb. per hour.

From p. 83 we have the relationship

$$\frac{1}{H} = \frac{1}{h_1} + \frac{1}{h_2} + \frac{1}{h_3}.$$

From the results of McAdams and Frost quoted on p. 89 the average value of h_1, the coefficient of heat transmission for the steam film, *i.e.*, between the condensing vapour and the metal wall, is 2400 B.Th.U. per square foot per 1° F. per hour which can be taken here. This, however, assumes no dissolved gas and therefore no gas film which would reduce the coefficient. To allow for this assume $h_1 = 1200$.

The coefficient of heat transfer for copper is about 200 B.Th.U. per square foot per 1° F. per hour for 12 inches of thickness. Assuming copper tubes in the condenser of 1/16 inch thickness, the value of h_2 becomes 38,400. (If iron tubes are used, then from Table VII the conductivity is 160/1000 = 1/6th that of copper. If the tubes are say 1/6th inch thick, the value of h_2 would be 2400.)

Regarding the coefficient of heat transfer between solid and liquid, it was remarked on p. 86 that there is little agreement between the results of various investigators. For the present purpose the expression proposed by C. S. Robinson (*J. Ind. Eng. Chem.*, 1920, **12**, pp. 644–6) may be used, which is

$$h_3 = 450\ V^{0\cdot 75}$$

where V is the linear velocity of the water in feet per second.

Thus if $V = 0\cdot 01$ feet per sec., $h_3 = 14$
$V = 0\cdot 10$ feet per sec., $h_3 = 80$
$V = 1\cdot 00$ feet per sec., $h_3 = 450$
$V = 2\cdot 00$ feet per sec., $h_3 = 760$

If we assume a water speed of, say, 2 feet per second, then $h_3 = 760$. Inserting the values of the three components in the expression given above, we have

$$\frac{1}{H} = \frac{1}{1200} + \frac{1}{38{,}400} + \frac{1}{760}$$

whence $H = 456.$

Since the mean temperature difference is 100° F. and the heat to be removed per hour when condensing is 483,000 B.Th.U., we have the necessary condensing surface by calculation

$$\frac{483{,}000}{100 \times 456} = 10\cdot 5 \text{ sq. ft. approx.}$$

Cooling Surface.—In considering the cooling surface we have liquid on both sides of the metal tube, and

Robinson's expression can be employed for illustrative purposes. Assume that the velocity of the condensed vapour along the tube is 0·1 foot per second, then $h_1 = 80$. Then we have the calculation for the coefficient

$$\frac{1}{H} = \frac{1}{80} + \frac{1}{38{,}400} + \frac{1}{760},$$

whence $H = 73$.

Since the mean temperature difference is 75° F. and the heat to be removed is 66,000 B.Th.U., the calculation for the necessary cooling surface is

$$\frac{66{,}000}{75 \times 73} = 12 \text{ square feet,}$$

whence the total surface required for condensing 500 lb. of steam per hour at 212° F. and cooling it to 80° F. with 5490 lb. of water entering at 50° and leaving at 150° F. is 22·5 square feet.

It must be understood that the above example is only intended to show the method of ascertaining the necessary surface if the values of the three coefficients are accurately known. In the above the variation of h_1, the coefficient for condensing vapour and solid (see p. 88), with the velocity has not been taken into account in order to avoid complications. References to the work done in this connection are given in Chapter VI on Heat Transfer. Hausbrand ("Verdampfen, Kondensieren und Kuhlen") gives values for the overall coefficient of heat transfer for varying velocities of vapour (steam) and cooling water for both the condensing and cooling operations in a condenser. These are very useful for estimating the necessary surface, and the whole book is interesting and instructive.

In the above example steam has been considered, but the designer is, of course, more interested in the liquids which are encountered in distillation. There is no doubt that different liquids have different coefficients of heat transmission, but our knowledge is very fragmentary. In this connection it will be remembered that when discussing the work of McAdams and Frost in Chapter VI (p. 89) it was remarked that they found the film coefficient to be 2400 for steam, 340 for benzene and 260 for carbon tetrachloride. When, however, these coefficients are divided by the thermal conductivity and by the fluidity of the respective liquids, the values obtained were 2240, 2500 and 1500 respectively. The eight-fold difference becomes a two-fold one. Unfortunately, although seven runs were made with steam, only one was made with CCl_4 and two with C_6H_6, but the experiments would seem to indicate that if thermal conductivity and viscosity are taken into account, the coefficient for various liquids would lie between certain limits under equal conditions. However, until a great deal more work on heat transfer is done, we must be content with empirical data backed with a knowledge of fundamentals as far as they will go.

Types of Condensers.—There are many different shapes and sizes of condensers, but for our purpose the following classification is sufficient :—

(1) Coil condensers.
(2) Tubular condensers.
(3) Open surface condensers.

Coil Condensers.—The coil condenser is the oldest and still a very common type in many industries. One form consists of a spiral tube of iron, copper, earthenware, lead, etc., totally immersed in water contained in a tank. Another form consists of straight lengths of tube placed parallel to one another and all connected into one continuous coil by means of return bends. This latter type, which is probably better known as a box condenser, is still much favoured in the petroleum industry.

From the point of view of heat transfer both these forms of condenser have several inherent faults, of which the most important is the low velocity of the water. This results in a very low rate of heat transmission, partly due to the water film on the tubes, which is scarcely affected by the slow-moving liquid, and partly because the dissolved air that separates and adheres to the pipe-surface is not swept away.

In the average worm or spiral condenser there is a dead space at the centre and, owing to the low water speed, there is opportunity for convection currents to be set up, resulting in the cold water at the bottom mixing with the hot water at the top, with consequent increased water consumption and lower condenser efficiency. Again, the speed at which the water rises in the average worm condenser tank is in the neighbourhood of $\frac{1}{8}$ to $\frac{1}{4}$ inch per second in the vertical direction. The slope of the tube, however, is not far removed from the horizontal. Consequently, although the vapour enters at the top and the water at the bottom, there is very little approach to true counter-current flow.

Some improvement is possible by filling up the dead space with a cylinder exposed on the inside to the air which incidentally assists the outer surface in keeping the water temperature down, although this benefit is small. Again, the water may be injected into the bottom through an elbow or bend on the inside, so that a swirl is produced in the opposite direction to the path of the vapours, thus giving a closer approach to counter-current flow. This may be accentuated by a simple, even home-made, water injector.

In the box condenser there is also dead space, but not necessarily of such importance as that in the case of the worm coil, so much depending on the spacing of the pipes forming the coil. The direction of the vapour flow is reversed in each length of pipe and is approximately horizontal, and since the water rises vertically, or roughly so, we have in this type a mixture of counter-current, parallel and even cross-current flow. Naturally the rate of heat transfer is very low.

In both forms of condenser it is advantageous to decrease the size of pipe from the inlet to the outlet of the coil, because as the vapour condenses its volume is reduced and the smaller pipe gives that high-vapour velocity which is so desirable for heat transfer. Obviously this change must be in steps, and a small but sometimes important point is to avoid any pocket by making a weld as shown in Fig. 22.

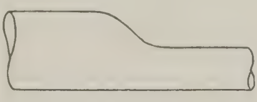

Fig. 22.—Weld in Coil.

In spite of these disadvantages, the submerged coil condenser remains a favourite with many distillers. In the first instance it contains a large volume of water, so that stoppage of the water supply from any cause may not be such a serious matter as it is with other condensers that depend on a rapid water circulation and contain only a small amount of water at any time. It is usually a simple matter to replace a worn-out worm condenser, but a tubular condenser requires a little more care. A box-condenser is an awkward piece of apparatus for repairs, especially if the very bottom row of pipes is affected.

Tubular Condensers.—The tubular condenser, as shown in Fig. 23, in its best known form consists of a number of straight, parallel tubes, the ends of which are expanded into tube plates which form the ends of a metal cylinder, the condenser body. The vapour may pass inside the tube with the water outside or *vice versa*, the latter course being adopted if the cooling water is very dirty. The insides of the tube can be easily cleaned by removing the end covers. If properly designed the tubular condenser is capable of giving much better heat transfer than the submerged coil, and for the condensation of equal amounts of vapour is much more compact.

The volume of water in the body is relatively small, and by means of suitable baffles it can be given a high velocity with resulting improvement in the heat transmission. Thus, as shown in Fig. 23, the vapours and water move partly in counter-current flow and with high velocity. In another type the water is guided in a spiral course by baffles which extend from the water inlet to the outlet and which are slipped over the parallel condenser tubes.

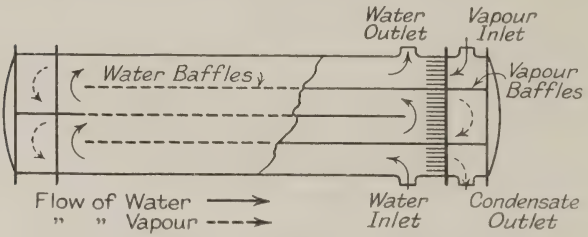

FIG. 23.—Tubular Condenser.

Tubular condensers may be either horizontal or vertical; probably the latter form is more generally employed. The partial or dephlegmating condenser is usually tubular and is simply a condenser which, as its first title implies, does not completely condense the vapour that enters it. There are many points in the design of both complete and partial tubular condensers, and especially of the use of the latter in connection with the fractionating column, which might be discussed, but these must be omitted on account of space limitations.

Surface Condensers.—In this type of condenser, Fig. 24, the vapours to be condensed are passed into a pipe-coil over the outside surface of which water is trickled. The utility of this type of condenser is not as fully appreciated in distillation work as it might be, for it is both economical in water consumption and also renders possible a high rate of heat transfer.

The flow of vapour should be downward, that is, vapour and liquid should travel in the same direction.

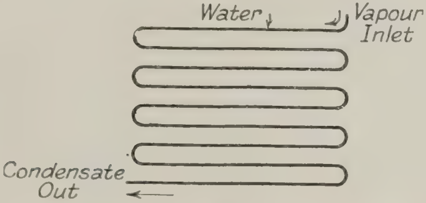

FIG. 24.—Open Surface Coil Condenser.

If they travel in opposite directions the downward flow of the liquid is impeded by the vapour, with the result that the rate of heat transmission is lowered on account of the thick film of liquid in the pipe. It would, of course, be desirable in some ways if the vapour could be introduced into the bottom of the coil, for then the flow of vapour and water would be more nearly counter-current and, still more important, non-condensible gases and air would be swept along more effectively than when the vapour flow is downward. As usually constructed with concurrent flow, the water is comparatively hot when it trickles over the lower tubes, and since the hot vapours are entering here a portion of this water may be converted into steam. This is advantageous in that latent heat is involved instead of sensible heat with, of course, a considerably smaller water consumption. In fact, there are many cases where a truly evaporative condenser would be of considerable service when water is costly. The author had occasion some time ago to estimate the saving that could be achieved by the substitution of evaporative for ordinary coil and tubular condensers owing to the possibility of a heavy charge instead of a free supply. The calculated reduction was surprisingly high, but as the contingency did not arise, the proof was not forthcoming. The evaporative condenser has found extensive use in steam condenser practice and to some extent in the petroleum industry. Its use could be usefully extended.

Heat Transfers in Condensers.—The design of condensers is usually effected by a consideration of the overall coefficient of heat transfer, since our knowledge of the three components is fragmentary, to say the least. As has already been noted, the coefficient for condensing vapour to solid in the case of benzene and carbon tetrachloride, 280 and 240 respectively, is much lower than that for steam, 2400 as found by McAdams and Frost. Although the eight-fold difference is reduced to two-fold if thermal conductivity and viscosity are considered, yet, assuming that the coefficients for the metal wall and the cooling medium remain the same, it is apparent that steam requires a smaller condensing surface *as far as rate of heat transfer is concerned.* On the other hand, the latent heats of steam, benzene and carbon tetrachloride are in the approximate ratios of 12 to 2 to 1. Similarly, the sensible heats of these three liquids are in the ratios of 1 to 0·436 to 0·201. A common error in the design of condensers for stills where steam distillation is used is to allow insufficient surface for the condensation of the steam in the mixture. Actually, although there is a greater speed of heat transfer for steam, the total number of heat units per unit weight to be transferred is considerably greater, and consequently a large condensing surface is necessary.

The overall value of the coefficient of heat transfer in the condensation of steam may vary between 100 and 1,000 B.Th.U. per hour per square foot per 1° F., depending on the velocities of the steam and water. Values of H between 200 and 400 are often used in this connection with a steam velocity between 7 and 10 feet per second. The value of H for organic liquids varies between 8 and 30 B.Th.U. per hour per square foot per 1° F.

Coolers and Heat Exchangers.—The type of apparatus used for coolers and heat exchangers is so similar that they can be considered together, since cooling is, of course, merely heat interchange between two liquids. It is true that in many continuous-working plants the feed is heated by the vapours from the still, but this type of apparatus can be considered as a condenser and need not be further discussed.

The submerged pipe-coil described as a condenser may be used as a cooler, but on account of the low velocities involved, is not highly efficient. The advantages of, in fact the necessity for, high velocities would appear to be very inadequately appreciated. Thus cooling apparatus is frequently seen in which the idea is to maintain a large body of the liquid to be cooled for as long as possible in contact with the cooling surface. Under such conditions an extremely low coefficient of heat transfer is to be expected, since stagnation is at a maximum.

In general, it should be an axiom in designing coolers and heat interchangers that small pipes should be used in preference to large and that fluid velocities should be high without however requiring excessive pressure to force the fluids through the apparatus. Counter-current flow should usually be used because the general purpose of a cooler is to discharge the liquid at the lowest temperature, except in those cases where a liquid may become viscous if cooled below a certain minimum temperature, when parallel flow may be preferable.

Tubular apparatus similar to those already described as condensers may be suitably employed as coolers. Double-pipe coolers and exchangers give excellent results. In these a tube carrying the liquid to be cooled is slipped inside another and larger tube, the cooling medium flowing counter-current in the annular space. High velocities of both liquids are possible, but if small-bore tubes are used as recommended above, the throughput is limited. With large quantities of liquid to be handled it is necessary to have a number of these double-pipe coolers, and the high cost involved may counterbalance the advantages. In such cases a cheaper and less efficient type may be preferable.

Heat Transfer in Coolers.—In considering coolers and heat interchanges the transfer of heat from liquid to solid and *vice versa* is primarily involved. The measurement of velocities is easily effected, for there are no complications such as exist in the case of a condensing vapour where the volume is continuously diminishing.

Yet it would appear that there is greater accordance and nearer agreement with practice in the results obtained by various investigators for condensing than heat interchange. The problem is so important that the lack of information available is lamentable. The value of the overall coefficient of heat transmission can be taken as low as 6 B.Th.U. per hour per square foot per 1° F. for submerged coil coolers up to $H = 55$ for double-pipe coolers, depending, of course, on the particular service and conditions.

Air as Cooling Medium.—Although water is used in the majority of cases for condensing and cooling, yet, as has been mentioned, it is often possible with continuous stills to utilise the ingoing feed for this purpose. Occasionally air is used, but in general is undesirable, for, on account of the low thermal conductivity of nitrogen and oxygen (see pp. 82, 87), the amount of cooling surface is enormously greater than that required when water is used. Not only is the capital cost of the plant much higher, but there is an increased difficulty in control, especially in the case of air-cooled partial condensers.

Distillation Details.—Having considered stills, columns and condensers, the largest and most obvious parts of a distillation apparatus, a few other matters can be discussed which are mostly essentials, but which are categorised as details for convenience only.

There are many matters other than good design which affect the efficiency and economical working of a still, especially where distillation is only one of the processes used in the production of a certain article. The results obtained in a still may be, and usually are, dependent on the efficiencies achieved in previous operations. Thus through carelessness or by accident, the concentration and the amount of impurities in the feed to a continuous still, or the charge of a discontinuous still, may be such that the working costs of distillation are considerably increased above normal good practice although the still itself may be worked with care and relative economy. It is not possible to discuss this aspect, but it is of great importance.

Again, the rate of distillation, the purity of the main fractions, the size of the intermediate fractions, in short, the distillation itself, is dependent on the design and the method of working. The distillation may be controlled from the laboratory, but in most cases a great deal if not all is left to the stillman. This aspect is discussed broadly on other pages and need not be further considered here.

The details remaining are those which might be called engineering ones, and concern such matters as the steam supply, pipe and valve arrangements, and so on.

Quality of Steam.—The steam supplied to the coils of a still should be as dry as possible if optimum heat transfer is desired. Water is a good heat insulator, and the admission of wet steam merely adds to the amount which must be produced by condensation in the coil and so increases the obstacle to heat flow. It is surprising how often a still is used, and in some cases intentionally, as a drain for a steam main. The belief behind this practice seems to be that the hot water will impart some of its heat to the boiling liquid in the still.

If the steam in the main is wet, it should be trapped before entering the coils. The very fact that the steam is wet points to insufficient lagging, bad draining or, going to the source, the boiler may be priming due to too high a water level or dirty feed. If the trouble is due to boiler feed, it points to returning the water from the steam traps to the boiler. In many works very little make-up is needed. Even the small amount of steam evolved by self-evaporation when a trap discharges can be saved by adding to the outlet some feet of piping, which thus forms a primitive air-cooled condenser. Up to 15 per cent. of this steam can be recovered in this way. The discharge pipe of steam traps should not be connected to a common main, but should drain into a cup—a reducing socket is handy—which is connected to this main. When the still is shut down a leaking coil, if not previously noted, can be detected by the discharge from the trap.

As already discussed, the use of superheated steam in coils should not be allowed, but a moderate superheat in the steam main is advantageous in long, straggling works, provided there is little superheat left by the time the still is reached. If the steam is too hot, a simple air condenser between the main and the coils may be used—assuming a moderate superheat, of course.

Arrangement of Valves and Pipes.—All valves in connection with a still should be conveniently located. It is absurd to expect a stillman to climb ladders and crawl over other plant to reach a particular cock or valve. It is possible to devise a standard arrangement of valves so that a man going to work a new still is soon familiar with the location of each control. This can be carried further by bringing nearly every control to one spot, preferably near the receiver into which the distillate discharges. Thus imagine a steam still and column with partial and final condensers working under vacuum. There are steam to coils, cold water to and hot water from the two condensers, mercury vacuum gauges, and so on. With a little thought a simple arrangement can be devised which is easily understood and involves little movement by the workman.

Considering the enormous number of pipes which are found in many works where distillation is carried out, it is astonishing how little thought is given to a reasonable arrangement. In many cases there is simply no attempt to avoid confusion, and the result is often chaos. Yet a little forethought will work wonders, but disentangling the mess is a slow and weary task.

The brief remarks on apparatus given in this and the preceding chapter can only touch on the fringe of a large number of interesting matters connected with distillation, each of which could be discussed at considerable length. Distillation under reduced pressure offers many interesting problems, such as size of vacuum pump, type of condensers, methods for the maintenance of any desired vacuum, and so on. The steam supply to continuously working columns is automatically regulated by ingenious apparatus, and it is now possible in certain cases to have these columns with automatic control so that changes in the feed will not affect the composition of the distillate. Again there is the wide field of works practice in small details to explore and discuss in works jargon. The metals to be used with different liquids would afford ample food for thought. These and similar matters cannot, however, be discussed.

CHAPTER IX

ETHYL ALCOHOL

ETHYL alcohol, C_2H_5OH, is the active constituent of intoxicating beverages and is commonly known as alcohol, although this is the generic name for compounds which are the hydroxides of hydrocarbon radicals. Alcohol can be formed synthetically from its elements carbon, hydrogen and oxygen, but in practice is obtained from three classes of materials. (1) Those containing alcohol. (2) Those containing sugar. (3) Those containing starch.

Materials containing Alcohol.—Brandy is prepared by the distillation of wine made by fermentation * of the juice expressed from grapes, the wine yeast necessary for this fermentation occurring naturally on the skins and stalks. The finest brandy comes from the neighbourhood of Cognac, France, where the grapes give a wine inferior for drinking purposes but excellent for conversion into eau-de-vie. Brandy can also be obtained by distilling the alcoholic solution made by passing water slowly through a series of tanks filled with marc, *i.e.*, the pulp of grape skins, wine yeast, pips, etc., remaining in the wine-press after the juice has been expressed.

Materials containing Sugar.—Sugar-beet, cane megasse or molasses, figs, amber cane and other materials containing sugar yield a dilute alcohol solution when they are fermented with yeast. In the case of molasses, a by-product of sugar manufacture, no special treatment is required before fermentation beyond dilution

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* Fermentation in its wider aspects includes chemical reactions brought about by minute living organisms or by certain products of animal or vegetable life. Yeast decomposes sugar into alcohol and carbon dioxide, and it is to be noticed that nearly half the original material is lost as CO_2 thus :—

$$\underset{180}{C_6H_{12}O_6} = \underset{92}{2C_2H_5{\cdot}OH} + \underset{88}{2CO_2}$$

in the ratio of 1 volume of molasses to 3 or 4 volumes of water and slight acidification with sulphuric acid to prevent the growth of moulds and bacteria which cause loss of sugar. In about two days after the addition of the yeast to the dilute solution, conversion of the sugar into alcohol is completed. The distillation of this dilute solution will be discussed later.

The sugar content of molasses varies from 48 to 60 per cent., with an average of 55 per cent. Each gallon of molasses yields about 0·43 gallon of 95 per cent. alcohol, or roughly 130 gallons per ton of sugar. In the case of sugar-beet, the average sugar content is 15 per cent. and the average yield of 95 per cent. alcohol is 21 gallons per ton of beets. The beets are sliced and the sugar is extracted by diffusion, the resulting solution being fermented as before. Beet molasses average 50 per cent. sugar and yield about 0·4 gallon of 95 per cent. alcohol per gallon of molasses.

Materials containing Starch.—A prominent source of alcohol is that of those materials which contain starch, such as corn, rice, potatoes, barley and wheat. Starch is a complex compound of the constitution $(C_{12}H_{20}O_{10})_{20}$ and will not undergo direct alcoholic fermentation. It must first be broken down into simpler carbohydrates, a process achieved by allowing the grain to germinate. During this process, which is called malting, the enzyme diastase is formed. This enzyme can dissolve an insoluble carbohydrate like starch and break it down into maltose and dextrin, compounds which on the addition of yeast are still further broken down and converted by fermentation into alcohol.

Corn contains about 65 per cent. starch and yields some 115 gallons of 95 per cent. alcohol per ton. Potatoes contain an average of 21 per cent. starch and 6 per cent. sugar. The yield is about 40 gallons of 95 per cent. alcohol per ton of potatoes.

Alcohol Distillation. The problem of alcohol distillation can be considered from two aspects, one the dehydration, since in every case the alcoholic solution is dilute, the other the rectification or removal of the by-products, most of which are formed during the fermentation, although some are produced by chemical action during the distillation itself.

Considering the first aspect, the separation of alcohol from water, it is remarkable that, although an enormous amount of work has been done and many books have been written on various aspects of spirit manufacture, yet there is a considerable amount of uncertainty regarding the relation between the composition of the mixture and of the vapour in equilibrium with it. Most writers use the figures experimentally obtained by Sorel (*Comptes rendue de l'Ac. des Sciences*) in 1892. Mariller ("La distillation fractionnée et la rectification," 1917), Hausbrand ("Die Wirkungweise der Rectifizier-und Destillier Apparate," 1921) and others make elaborate calculations based on Sorel's data, which they consider most reliable. Lewis (*J. Ind. Eng. Chem.*, 1920, **12**, p. 496), after pointing out the serious discrepancies between the figures of Groenig, Duclaux, Sorel and Evans, considers the results obtained by Wrewsky (*Zeit. physikal. Chem.*, 1912, **81**, 1) most reliable. Wrewsky did not work at constant pressure but at constant temperature, and Lewis makes use of these data by recalculating the results, extrapolating up to the boiling point. The boiling-point curve was taken from the results of Noyes and Warfle (*J. Amer. Chem. Soc.*, 1901, **23**, p. 154).

If the problem of alcoholic distillation is to be studied adequately, and if the methods of design described in Chapters III and IV are to be of service, it is essential that the relationship between the composition of vapour and mixture should surely be accurately known. Yet such is not the case. On the other hand, there is accuracy regarding the composition of the constant boiling-point mixture of alcohol and water which Young and Fortey (*Trans. Chem. Soc.*, 1902, **81**, p. 717) found to be 95·57 per cent. alcohol by weight and Wade and Merriman (*ibid.*, 1911, **99**, p. 997) determined as 95·59 per cent., the small difference being insignificant for all practical purposes.

In the first and sixth columns of Table IX are reproduced Sorel's figures for various alcohol mixtures and the vapour in equilibrium, while in the seventh column are given those of Lewis for the vapour composition corresponding with the same mixtures, as read from the graph that he has drawn. Considerable difference between the figures in the sixth and seventh columns will be noticed. The second column gives the boiling points of the mixtures under 760 mm. after Sorel. The third column gives the number of Calories produced on mixing alcohol and water in the proportions given in the first column. The fourth and fifth columns give the sensible heat and latent heat of 1 kg. of the mixture as given by Mariller ("La distillation fractionnée et la rectification," 1917, pp. 442–5).

In using the methods of design described in Chapters III and IV, the introduction of heats of combination would make the calculations very involved. Since the size of the working column is derived from that of the perfect column by multiplying by a factor, and as this factor includes the various effects which cause divergence from theory, there is little point in complicating matters. The figures for the heat of combination are included as a matter of interest and to indicate the general order of their magnitude for different mixtures, but may otherwise be neglected without great error. The important data are the relationships between liquid and vapour composition and, as has been remarked, there is considerable uncertainty regarding the correct figures.

The latent heat of vaporisation can be taken at the mean temperature of the column, as already stated (Chapter III).

TABLE IX

Ethyl Alcohol and Water

		LIQUID. Heat in 1 kg. in Calories.*			VAPOUR. Alcohol per cent. by wt.	
Alcohol per cent. by wt.	B. p. in ° C.	Heat of combination.	Sensible heat from 0° C. to b. p.	Latent heat.	Sorel.	Lewis.
0·00	100·00	0·00	100·50	536·50	0·00	0·00
2·00	97·73	1·34	103·21	529·95	17·45	15·00
4·00	95·81	2·53	106·15	523·40	29·62	31·50
6·02	94·12	3·59	107·10	516·79	37·17	47·00
8·05	92·63	4·56	106·54	510·14	43·47	53·50
10·51	91·12	5·62	105·32	502·08	50·07	58·50
12·15	90·24	6·27	104·44	496·71	53·70	60·70
13·80	89·44	6·88	103·65	491·31	56·28	62·70
16·28	88·38	7·72	102·19	483·19	58·49	64·80
17·95	87·75	8·21	101·28	477·72	59·33	66·20
20·46	86·88	8·84	100·07	469·60	60·33	68·00
22·14	86·35	9·16	99·36	463·99	60·87	68·80
23·84	85·87	9·40	98·75	458·33	61·43	69·80
26·40	85·27	9·61	97·78	450·01	62·25	71·30
28·13	84·92	9·66	97·19	444·38	62·82	72·10
29·86	84·60	9·67	96·66	438·75	63·43	72·80
32·50	84·20	9·58	95·83	430·07	64·31	73·80
35·18	83·82	9·34	94·92	421·29	65·21	74·50
37·90	83·43	9·02	93·78	412·38	66·21	75·30
39·73	83·17	8·79	92·87	406·35	66·89	75·80
42·52	83·81	8·41	91·27	397·25	67·88	76·40
45·37	82·45	7·96	89·46	387·92	68·93	77·00
47·29	82·23	7·64	88·08	381·63	69·65	77·20
50·21	81·91	7·14	86·23	372·05	70·74	77·80
52·20	81·71	6·80	85·16	365·55	71·50	78·10
55·21	81·43	6·26	83·68	355·69	72·68	78·60
57·25	81·25	5·90	82·86	349·01	73·49	79·00
60·38	80·98	5·34	81·63	338·76	74·80	79·60
62·49	80·80	4·98	80·92	331·85	75·79	80·00
65·73	80·53	4·46	79·93	321·24	77·40	81·00
66·83	80·44	4·29	79·61	317·63	77·92	81·20
70·17	80·17	3·78	76·68	306·70	79·50	82·20
72·45	79·99	3·46	78·06	299·39	80·70	83·20
74·75	79·82	3·15	77·32	291·70	81·95	84·00
77·09	79·66	2·85	76·35	284·07	83·19	85·30
79·50	79·49	2·57	74·75	276·14	84·51	86·00
81·95	79·33	2·30	70·88	268·12	85·92	87·00
84·46	79·18	2·04	65·94	259·90	87·37	88·40
87·06	79·03	1·80	62·94	251·25	89·11	89·54
89·71	78·89	1·55	60·60	242·74	90·74	91·12
92·46	78·75	1·28	58·98	233·70	92·95	93·03
95·34	78·61	0·96	57·54	224·52	95·52	95·38
96·84	78·54	0·76	56·95	219·35	96·84	96·83

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* One Calorie, or "great Calorie," is the amount of heat required to raise 1 kg. of water 1° C. from 15° C. One calorie, or "small calorie," is the amount of heat required to raise 1 gram of water 1° C. from 15° C. One Calorie = 1000 calories.

The primary fractionation of dilute alcoholic solutions is not difficult, since the temperature and composition steps are great relatively to those which hold when the constant boiling-point mixture is approached. The figures show that the enrichment is rapid at first, but decreases with increasing concentration. The most important part of the fractionation, and therefore of the design, is that connected with the enrichment near the constant boiling-point mixture, and the chief duty of a column is the final enrichment up to the maximum possible.

Removal of Impurities.—The other aspect from which the distillation of alcohol can be considered is that of the removal of the impurities, a matter which is given consideration in the companion book ("Distillation Principles," pp. 119 *et seq.*) to this, and which can be summarised as follows. Barbet ("La Rectification et les colonnes rectificatrices," 1895, p. 42) established a coefficient of purification

$$K = \frac{\text{Per cent. impurities in the alcohol in the distillate}}{\text{Per cent. impurities in the alcohol in the mixture}}.$$

It must be made perfectly clear that this refers to the per cent. impurities in the alcohol as alcohol and not to the per cent. impurities in the mixture of alcohol and water. Sorel obtained data in connection with the latter which Barbet converted into the form required for the coefficient K by simple calculations. In Table X are given these calculated values of K for various impurities found in alcohol.

It is seen from Table X that when K is greater than 1, the alcohol vapour is richer in the impurity than the alcohol in the liquid; when $K = 1$, the amount of the impurity is the same for both liquid and vapour, and when K is less than 1, the impurity concentrates in the liquid. As the concentration rises the value of

TABLE X

Values of K *for Various Alcohol–Water Mixtures*

Alcohol per cent. by wt.	Amyl alcohol.	Ethyl formate.	Methyl acetate.	Ethyl acetate.	Ethyl iso-butyrate.	Ethyl iso-valerate.	Amyl acetate.	Isoamyl iso-valerate.
0·8	3·30							
8·05				5·67				
20·46	2·02			5·43				
24·69	1·30			5·43				
33·39	1·05		5·83	4·77				
42·52	0·80		5·26	3·86			1·866	
52·20	0·615	8·0	4·92	3·3	3·23	1·76	1·307	1·0
62·49	0·44	7·26	4·61	3·07	1·96	1·45	0·94	0·7
73·58	0·36	6·6	4·25	2·77	1·30	1·20	0·74	0·463
85·76	0·26	5·68	4·01	2·37	1·07	0·882	0·588	0·343
92·46	0·22	5·08	3·78	2·09	0·897	0·797	0·548	0·299

K falls, showing that the ratio of the impurity to the alcohol in the liquid and vapour is decreasing. In actual practice there is always more than one impurity present, and these impurities have a mutual influence which affects the value of *K*. Moreover, in Sorel's original work the amount of impurity present in the original liquid never exceeded 2 per cent., whereas in practice the concentration of some of the impurities considerably exceeds this amount at certain stages of the rectification. Nevertheless, this consideration supplies a reasonable, if not an exact, explanation of the actual occurrences in a still or column as regards the impurities.

From whatever source it is obtained, the dilute alcohol solution contains, in addition to its two main constituents, a considerable amount of solid matter in suspension, various salts in solution and the volatile impurities discussed above. The first step is a preliminary distillation to remove the solid matter and some of the water, a 5 to 10 per cent. mixture or mash being concentrated to about 38 or 40 per cent. as a maximum. This may be carried out in either a discontinuous or continuous working still. The impure partly concentrated alcohol contains organic acids which would react with the alcohols present to form esters, and before rectification these acids are neutralised with alkali, soda ash or caustic soda. This neutralisation is never completed because, if the solution is alkaline, the nitrogenous bodies present liberate amines which give an unpleasant smell to the alcohol.

Considerations of space preclude a detailed analysis of the individual impurities, but the following will probably indicate how the knowledge of the value of K is useful in explaining the actual occurrences. In the case of amyl alcohol, $K = 1$ where the solution contains about 33·4 per cent. alcohol, consequently the alcohol in both vapour and liquid contains the same amount of impurity. In discontinuous fractionation, the concentration at any point changes continuously, and amyl alcohol will be more concentrated at that point in the column where there is 33·4 per cent. alcohol. To keep it as long as possible in the lower parts of the column, the alcohol concentration is kept at the maximum on the upper plates. As distillation continues, the point where the strength is 33·4 per cent. rises up the column, and the distillate contains an increasing amount of amyl alcohol. In the case of continuous distillation where the concentration at a point is constant the impurity tends to concentrate where there is 33·4 per cent. alcohol. In the continuous type of still mostly used, the impurities are allowed to concentrate at various points and are drawn off periodically or continuously as will be discussed shortly.

Alcohol Stills.—Starting with a dilute solution, two stages in the production of a high-strength alcohol can be recognised. In the first operation the non-volatile impurities are eliminated, and the amount of water considerably reduced, while some of the impurities can be separated. In the second stage, the partly concentrated liquor is rectified, the remaining water being removed up to the constant boiling point, while the volatile impurities are more or less separated according to the degree of purity required.

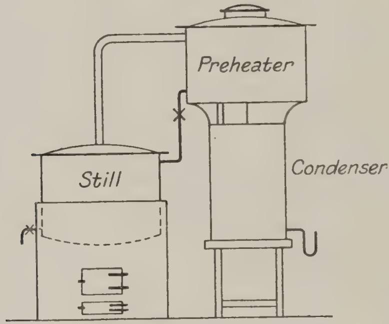
The distillation may be effected discontinuously by repeated fractionation, but, as will be seen shortly, this is tedious and costly, though still employed under certain circumstances. Great economy in time and fuel can be obtained by the adoption of continuous working. The rectification also can be either discontinuous or continuous, the choice depending on the daily quantities to be handled and other circumstances (see pp. 66–67). In some cases the continuous still for the preliminary concentration is separate from the continuous rectifying apparatus, the distillate from the former being condensed and fed to the latter as required. In other cases, the concentrating and rectifying stills form one complete unit.

Discontinuous Distillation.—In the manufacture of brandy, whisky and rum, the impurities produce characteristic odours and tastes, so that complete removal is not desired. On this account, simple pot stills are often employed heated by direct fire or steam. The vapours pass out of the still and almost directly into the condenser, so that there is very little partial condensation and therefore fractionation.

Brandy.—Such a simple still is shown in Fig. 25 and is a type such as is used in the manufacture of Cognac brandy. To effect fuel economy a preheater (chauffe-vin) is often used, so that a fresh charge can be warmed up by the vapours from the still before they pass to the condenser. The following is typical of the method of working such a still.

At the beginning of the operation the still and preheater are charged with wine. If the charge is 1000 litres (220 gallons) of wine containing, say, 8 per cent. alcohol by weight, boiling will occur in some 2½ hours.

Distillation is effected in a slow and regular manner, this being necessary to ensure a high-class brandy, but towards the end of the operation the rate of heating can be increased. The distillate called *brouillis* is collected over a period of nine to ten hours, measures 300 to 350 litres (66 to 77 gallons) and contains 20 to 24 per cent. alcohol by weight. The residue (*vinasse*), almost exhausted of alcohol, is run off and the fresh preheated charge run into the still. This boils in about half an hour, the vapours being utilised as before in warming up another charge in the preheater.



Brandy Still.

FIG. 25.—Brandy Still.

After three distillations in this way, some 1000 litres of *brouillis* are obtained, which are fed into the still and distilled like the weaker solution. In this case, however, the distillate is collected in fractions in order to separate the brandy from higher alcohols and ethers present in the *brouillis*. The first fraction (*heads*) measures 3 to 5 litres (0·66 to 1·1 gallons) and is rich in aldehydes and ethers. It is collected for addition to other *brouillis*, or until there is enough to make up a still charge. The second fraction (*the heart*) is collected over some 10 to 11 hours, measures 360 to 380 litres

(80 to 84 gallons) and contains about 60 per cent. alcohol by weight. The third fraction (*tails*) measures some 200 to 225 litres (44 to 50 gallons) and contains from 16 to 20 per cent. alcohol by weight. The whole distillation occupies 16 to 18 hours.

By addition of a simple partial condenser which produces a reflux, a brandy containing anything from 40 to 68 per cent. alcohol by weight can be obtained by one distillation, and by a rectification the strength can be increased to 80 per cent. As, however, increases in alcoholic strength and fuel economy are obtained at the expense of flavour, the more costly method of distillation is often preferred in the Cognac area.

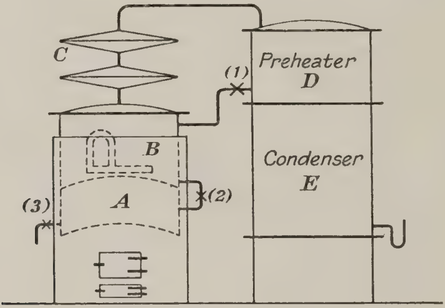
Whisky.—In whisky manufacture the pot still is sometimes employed, usually with some simple form of partial condenser such as a water-jacketed still-head or pipe between the still and the condenser proper. The stills are very much larger than those described for brandy, capacities up to 15,000 and 20,000 gallons being found. As in the case of brandy, the pot still is useful in that a considerable amount of the impurities is retained to give the beverage a characteristic odour and taste.

In making Scotch whisky two distillations are effected, the dilute wash being distilled to yield a low wine which is again distilled. In the final operation three fractions are obtained, (1) foreshots, (2) whisky, (3) feints. Fractions (1) and (3) contain the various secondary products and are added to the low wines for redistillation. The middle fraction is that used for consumption and contains 60 to 75 per cent. of alcohol by weight. Scotch whisky has a characteristic flavour derived partly from the peat used in drying the malt.

Irish whisky involves three distillations, and there is also a more complex classification of the fractions, *e.g.*, strong and weak low wines, strong and weak feints.

The strength of the whisky fraction is about 80 per cent. of alcohol by weight.

Discontinuous Rectification.—The simple stills described give an alcohol which is not sufficiently pure for many uses. To produce a high-strength alcohol with only small amounts of impurities a very efficient fractionating column is needed. For small daily outputs a discontinuous apparatus can be used, but even when this is very efficient, the amount of actual high-grade alcohol obtained is not much more than a quarter of the charge in the still. The remainder of the distillate is more or less contaminated with the various impurities. To produce a high-grade alcohol the most satisfactory type of still is the continuous-working one.



Multiple Still.

Fig. 26.—Multiple Still.

Multiple Stills.—In some districts where brandy is made, the distillation apparatus, Fig. 26, comprises (1) a still divided into two chambers by a horizontal partition provided with a simple bubbler so that the vapours from the lower part, *A*, bubble into and boil the liquid in the upper portion, *B*, (2) a simple partial condenser, *C*, (3) a preheater, *D*, and (4) a condenser, *E*.

When starting the apparatus, the vessels *A* and *D* are charged with the weak alcoholic solution and the liquor in *A* is distilled. When the mixture in *A* has become low in alcohol the warm charge in *D* is run into *B* and *D* is recharged. The vapours from *A* condense in and boil the liquor in *B* until it also becomes weak in alcohol. *A* is then emptied, *B* run into *A*, *D* into *B* and *D* is recharged. The operation can be repeated as often as necessary and can be made continuous by keeping the cocks 1, 2 and 3 slightly open. Under these latter conditions the distillation is a very simple case of a continuous-working column and gives greater enrichment of the distillate, economy in fuel and saving in time.

Continuous Concentration.—As already stated, the elimination of non-volatile impurities and the reduction in volume of the water can be effected in a continuous working column, and such an apparatus is shown diagrammatically in Fig. 27. The fermented wash flows from the reservoir, *A*, through the heat interchanger, *B*, where its temperature is raised by the hot exhausted liquid flowing from the bottom of the column. From *B* the wash, raised almost to the boiling point, enters the column at *C* and flows down, meeting the steam introduced at *D*. In the figure it will be noticed that there are several plates above the feed-plate which are not always included but which give a small fractionating effect. The vapour from the top of the column passes to the partial condenser, *E*, which provides the main volume of reflux to the column, the uncondensed vapour being completely liquefied in the final condenser, *F*. The rate of flow of the concentrated solution is regulated at the outflow, *G*, so that if for any reason the condenser, *E*, does not condense enough vapour, the reflux to the column is maintained at constant volume by additional liquid from *F* as shown by the connections.

The wash often contains materials which form incrustations on the tubes of heat interchangers, and in such cases a recuperator such as is shown cannot be employed because the tubes cannot be cleaned on the outside, although there is no difficulty with the insides. Instead of a recuperator the wash may be passed through the partial condenser, *E*, which thus becomes a heat interchanger. If the vapours from the column pass outside the tubes and the wash inside, the tubes can easily be cleaned by removing the top and bottom covers of the condenser. The outsides of the tubes then need no attention.

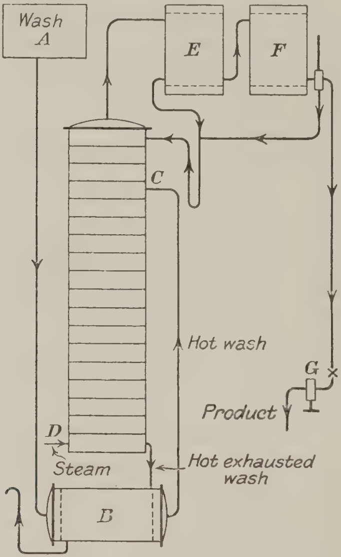


FIG. 27.—Continuous Still.

The strength of the solution leaving the final condenser will be between 38 and 40 per cent. alcohol by weight, and this liquid can then be continuously rectified in a plant now to be described.

Continuous Rectification.—The concentrated liquor can be rectified in a continuous plant such as is shown diagrammatically in Fig. 28. From the tank, *A*, the mixture passes through the recuperator, *B*, and enters the column *C* at *D*. Steam enters the column at *E*, and, bubbling up through the descending liquid, liberates, the head products, which are partly deprived of the alcohol accompanying them by fractionation on the plates above the feed-point, *D*, and are dealt with in

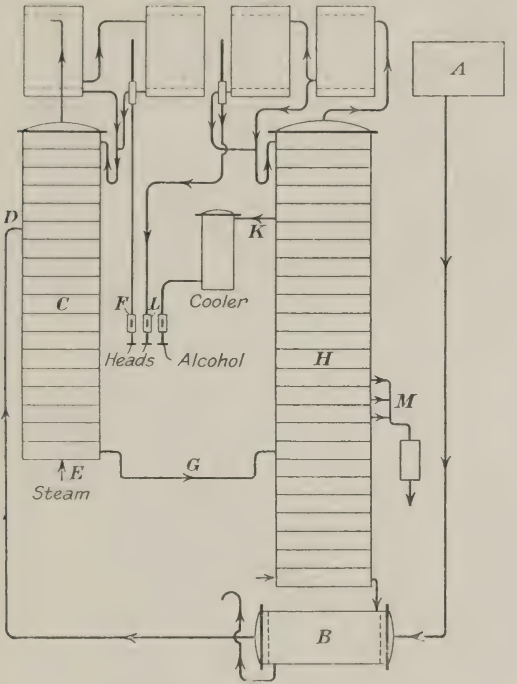


Fig. 28.—Continuous Rectifier.

the two condensers shown, the distillate being collected at *F*.

The solution leaving the bottom of the column *C* contains practically all the tail products (amyl alcohol, etc.), very little of the head products, but less alcohol than the feed, since a certain amount is mixed with the head products leaving the top of the column. This hot liquid flows by the pipe, *G*, into the column *H*, where it is fractionally distilled, the necessary heat being supplied in the form of steam introduced into the bottom of the column. The waste water freed from alcohol flows from the column through the heat interchanger, *B*, and thence to the drain. The alcohol is run off at the point *K*, which, it will be seen, is several plates below the top of the column, a point which will be discussed. Head products, partly freed from alcohol by the rectifying effect of the plates above *K*, pass to the condensers above and are collected at *L*. Impurities (tails) of the amyl alcohol class accumulate on the plates and are drawn off at *M* as shown.

Pasteurisation.—The withdrawal of the alcohol at a point lower than the top of the column is termed pasteurisation and the arrangement is credited to Barbet. The head products are more volatile than alcohol and consequently in a column working continuously and with constant composition at any point the volatile impurities tend to accumulate in the upper plates. By drawing the alcohol off as described, a much purer product can be obtained, since the impurities are on the plates above *K*.

Combined Concentration and Rectification Plant.—It is possible to combine the two preceding types of distillation plant so that there are constantly evolved four different products, (1) pure alcohol, (2) head products, (3) tail products, (4) alcohol-free exhausted wash. The foregoing descriptions are probably sufficient to enable the principles on which these more elaborate stills are designed to be appreciated.

Coffey's Still.—The Coffey continuous still (Fig. 29) is one well known in this country and consists essentially of two columns, *A*, the analyser, and *B*, the rectifier. Both columns are made up of wooden chambers braced together in an iron frame and separated by perforated copper plates provided with the usual overflow pipes the ends of which are sealed in a cup on the plate below.

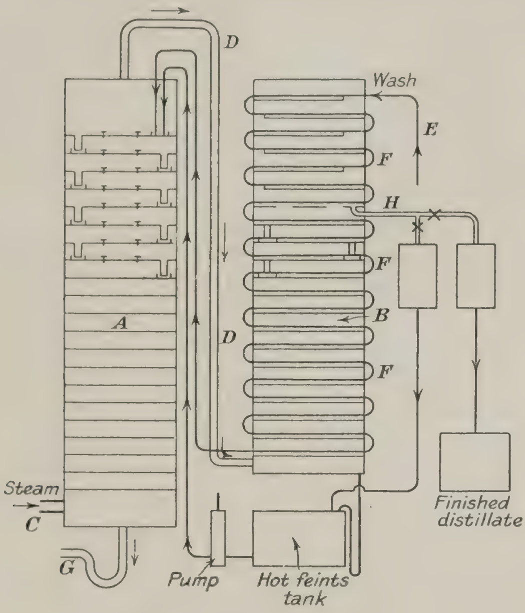


Fig. 29.—Coffey Still.

In starting up, steam is passed into the analyser, *A*, by the pipe *C* and passes from the top of *A* through the pipe *D* into the rectifier *B*. When the columns are full of steam, the wash is pumped through the pipe *E* into the zigzag pipe *F*, which enters the rectifier at the top, passes through each chamber in succession to the bottom and thence rises to the top of the analyser as shown. The wash passing through this pipe is heated almost to boiling and when delivered on to the top plate of *A* flows down the plates of this countercurrent to the ascending steam. The liquid overflows down the sealed pipes and the steam bubbles through the perforations in the plates. The wash has been deprived of its alcohol by the time that it has reached the bottom of the analyser and escapes by the trapped pipe *G*.

On reaching the top of *A* the mixture of alcohol and water vapours passes through the pipe *D* into the base of the rectifier and ascends through the perforated plates therein, bubbling through the reflux provided by the coil through which the wash is passing. Consequently the rising vapour becomes richer in alcohol as it ascends the rectifier, and at a certain level where the temperature corresponds with the condensation temperature of strong alcohol an unperforated copper plate (the spirit or dumb plate) is fitted. This plate is pierced by a wide pipe or pipes which stand 1 to 1½ inches above it and through which the vapour passes. The liquid on this plate is removed by a pipe, *H*, and can flow through a branch into a condenser and thence to the " finished distillate " receiver. At the beginning and end of a distillation (which normally lasts two or three days without intermission) weak spirit condenses and is run through the other branch of the pipe *H* to the condenser and thence to the " hot feints " receiver below.

The condensate from the base of the rectifier also passes to the hot feints tank, whence it is pumped to the top of the analyser. Fusel oil (amyl alcohol, etc.), which condenses at a higher temperature than alcohol, is easier liquefied and with some spirit and water comprises this condensate. At the top of the rectifier is a vapour pipe which carries off the spirit vapours not condensed by the pipe *F* conveying the wash, and also the more volatile impurities or heads, these mixed vapours passing into the condenser and thence to the "hot feints" tank.

It will be noticed that the heads and tails are not removed from the system but accumulate on the plates. If very pure alcohol is required, the condensate from the top of the rectifier should not be returned to the analyser through the "hot feints" tank but condensed and treated separately. The higher alcohols could be withdrawn from that point where they tend to accumulate, but this is rarely done in England. There is no doubt that the efficiency would be increased if the reflux were supplied by a partial condenser as described with the other stills, for this reflux would then descend through the whole of the plates, giving a greater scrubbing effect.

CHAPTER X

PETROLEUM

PETROLEUM is essentially a mixture of hydrocarbons of a few series mixed with smaller amounts of other hydrocarbons containing sulphur, nitrogen and oxygen, which are to be regarded as impurities. Three broad classes of the oil can be recognised according to the qualitative chemical composition as follows :—

(1) *Paraffin Base Oils.*—These oils yield solid hydrocarbons of the paraffin series which form what is commonly known as paraffin wax. There are obtained high yields of gasoline and also valuable lubricating and cylinder oils. Paraffin base oils are usually distilled with care to avoid cracking or decomposition by heat.

(2) *Asphaltic Base Oils.*—These oils on distillation leave as a residue a heavy asphalt or pitch mainly composed of the hydrocarbons of the naphthalene series. The yield of light products can be increased by " cracking " distillation in which conditions are so adjusted that the higher hydrocarbons are thermally decomposed to a moderate extent.

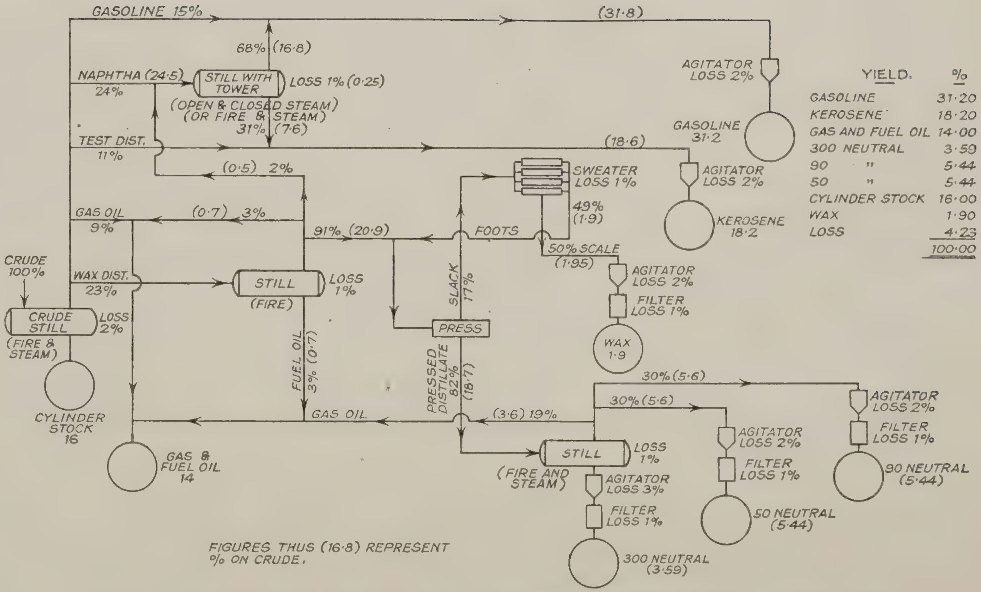
(3) *Mixed Base Oils.*—As the name implies, these oils contain both paraffin and naphthalenes and, broadly speaking, are refined by a combination of the two processes, cracking and non-cracking distillation.

A detailed description of all the various processes employed in the complete refining of the above classes of crude oil is beyond the scope of this book. Moreover, the description would have to be interpreted with much latitude, for the crude oils, especially mixed base oils, differ widely in their composition and properties, and each refinery evolves methods and plants which best suit the circumstances and the ideas of those in charge. Even a paraffin base oil may be refined by a combination of cracking and non-cracking distillation. It would perhaps be useful briefly to consider these two methods of distillation.

Non-cracking Distillation.—Non-cracking distillation has as its object the production of a maximum amount of high-grade lubricants, and the crude oil is distilled with fire and steam, a method which is often called "running to cylinder stock." As previously mentioned, a paraffin base crude is usually distilled by a non-cracking distillation, and it is convenient to discuss the method as applied to an oil of this kind. In this connection Fig. 30 will be found useful, in which is shown diagrammatically the number of distillations and other processes which make up the complete series of operations in a refinery working on such a crude oil.

The oil is charged into horizontal stills of 25 to 165 tons capacity (0·14 ton = approx. 1 American barrel = 42 American gallons. One British gallon = 277·418 cu. in. = 1·20094 American gallons. 1 American gallon = 231 cu. in.) heated by fire and provided with perforated steam coils placed near the bottom of the still. As soon as the oil is at a higher temperature than that of boiling water, the steam is admitted through the coils. This use of steam allows the distillation to proceed at a much lower temperature than without its use, thus at the start the temperature may be 100° F. and at the end 180° to 225° F. less than if the heating were by fire alone. This lower temperature to a great extent avoids thermal decomposition of the hydrocarbons of high molecular weight.

Various fractions may be taken. Thus in Fig. 30 a preliminary gasoline fraction has been taken. The second fraction is crude naphtha, which is distilled in stills provided with towers and heated by open and closed steam coils or sometimes by fire and open steam coils. The fractions from this still are as shown. Chemical treatment may be used before distillation



YIELD.	%
GASOLINE	31·20
KEROSENE	18·20
GAS AND FUEL OIL	14·00
300 NEUTRAL	3·59
90 "	5·44
50 "	5·44
CYLINDER STOCK	16·00
WAX	1·90
LOSS	4·23
	100·00

FIG. 30.—Flow Sheet, Parrafin Bane Oil. Non-cracking Distillation (From Bell.)

with the object of removing unsaturated hydrocarbons which might impart an unpleasant odour.

The wax distillate from the crude still is again distilled, but without or with very little live steam, so that slight cracking occurs, which converts the wax from a colloidal to a crystalline form. The resulting cracked distillate is chilled and filter-pressed to separate the crystalline wax from the residual oil. This residual oil is then distilled with fire and steam, the distillate being as shown in the figure. Typical yields from a crude paraffin base oil are given in the same figure.

Cracking Distillation.—In cracking distillation the crude oil is distilled from a fire still, but steam is only admitted very sparingly if at all. This method, which is often called "running to coke," is frequently employed for mixed base oils which contain so much asphalt that satisfactory cylinder oils cannot be obtained. The high temperature to which the still contents are allowed to rise causes decomposition, and the higher hydrocarbon molecules break down, forming simpler molecules which when condensed are liquids of lower boiling points. Gases and free carbon are also developed. Cracking distillation must not be confused with the cracking processes, and is used when a maximum quantity of gas, naphtha and burning oil is required rather than neutral oils and cylinder stock. Fig. 31 shows diagram-

TABLE XI

	Non-cracking distillation. Per cent.	Cracking distillation. Per cent.
Gasoline	20–30	25–35
Burning oils	8–12	15–25
Gas and fuel oils . . .	40–50	30–40
Lubricating oils . . .	2–6	2–5
Wax tailings . . .	—	1
Coke	—	4–5
Loss	4–5	4–6
Miscellaneous . . .	5–10	

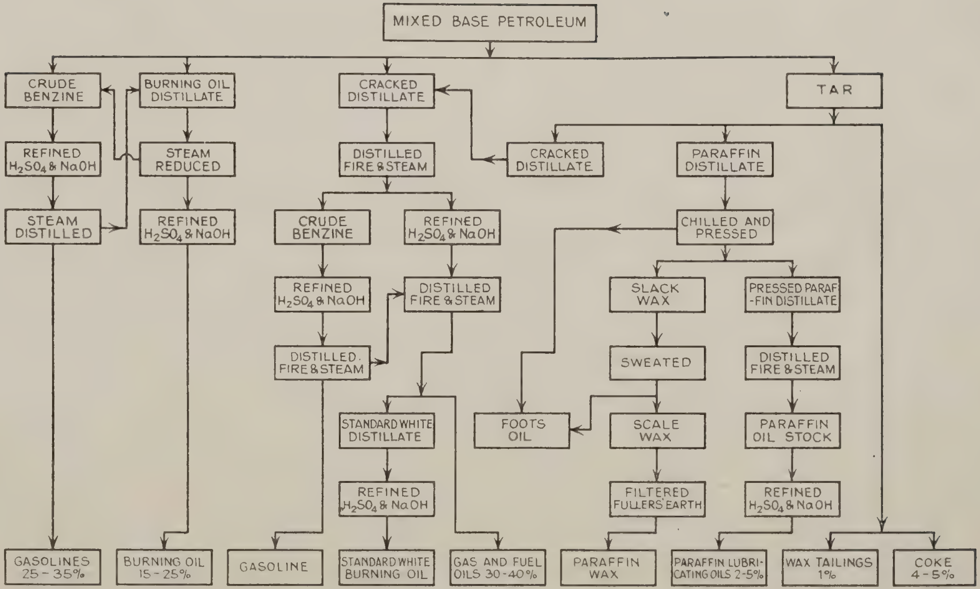


FIG. 31.—Flow Sheet, Cracking Distillation.

matically the various processes in a cracking distillation of a mixed base oil.

As already remarked, the employment of cracking or non-cracking distillation depends on various circumstances. In Table XI is given a comparison of the results obtained when a mixed base oil is treated by the two methods.

Asphalt Base Oil Distillation.—The treatment of these oils can be briefly outlined. The distillation is not carried further than is necessary to obtain a reasonable fuel oil. The yield of products depends, of course, on the original crude oil, but the following is typical of California petroleum :—

Gasoline	13·5 per cent.
Kerosene	5·0 ,,
Various	10·0 ,,
Residual fuel oil . .	71·5 ,,

The removal of the lighter distillate or "skimming" is usually effected in "topping" plants such as will be described.

If, however, there is present a greater amount of lighter oils a series of operations are carried out as shown in Fig. 32, which represents the practice in many cases. The yields obtained per ton are given on this figure and can be compared with those in Table XI.

The foregoing account is necessarily brief and incomplete, but may be sufficient to enable a general idea to be gained of the main operations of a refinery. Attention will now be given to the stills themselves.

Fired Stills.—Consider first the batch type of still, which is even now a common type. These stills are of the horizontal cylindrical type of 25 to 165 tons capacity, a typical design being shown in Fig. 33. The bottom plate for the smaller sizes is usually in one piece running along the whole length in order to avoid exposure of a riveted joint to the hot flue gases. For such stills the

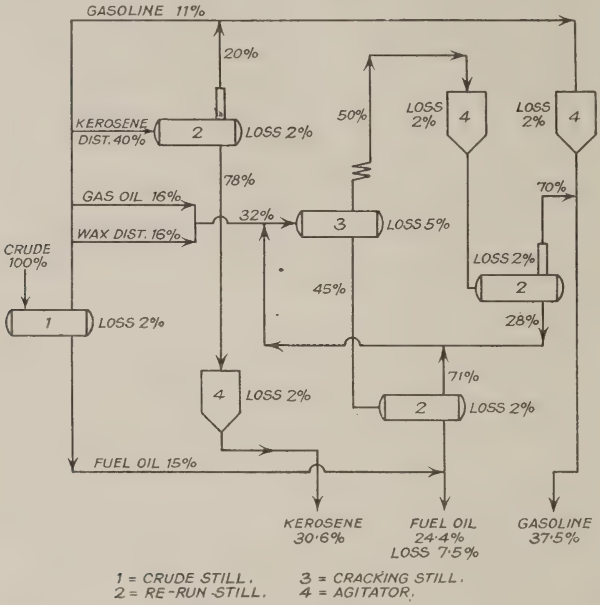


Fig. 32.—Skimming Process with Cracking.

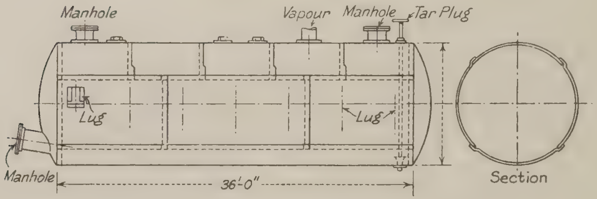


Fig. 33.—Fire Heated Petroleum Still.

plate thickness would be $\frac{1}{2}$ inch for the bottom and $\frac{3}{4}$ inch for the rest of the shell. For larger sizes two or more plates are needed and their thickness may be $\frac{5}{8}$ or $\frac{3}{4}$ inch, occasionally 1 inch, while the rest of the still may be $\frac{3}{8}$ to $\frac{1}{2}$ inch plates. The stills are carried by lugs riveted to the sides and resting on concrete piers, which are protected by the fire-brick from the hot gases playing on the still bottom and sides. One end of the still is supported 6 inches or so above the other end to facilitate removal of the residue if liquid. Manholes are provided on top and one at the end, the latter being of ample dimensions if " coke " has to be removed.

The following table gives the dimensions and capacities for various sizes :—

TABLE XII

Horizontal Cylindrical Stills

Charging capacity. Tons.	Total capacity. Tons.	Dia. Feet.	Length. Feet.	Vapour pipe dia. Inches.	Evaporating surface. Sq. feet.
25	30	8	24	8	128
50	60	10	30	10	200
85	100	12	36	12	288
138	160	14	42	14	392
165	200	15	45	15	450

According to Bell (" American Petroleum Refining "), " an analysis of the records of many still runs shows the amount distilled to vary between 1·27 and 1·71 gallons per hour per square foot of evaporating surface, with an average of 1·50. This figure allows 6 per cent. of idle time for charging, pumping out, etc., and may therefore be used directly for estimating the operating results over an extended time." " The evaporating surface for the usual type of horizontal cylindrical still may be taken as 2/3 of the diameter multiplied by the length when the still is operated on the batch principle. This figure 2/3 will allow for the reduction in area of the evaporating surface as the oil level drops in the still." Multiplying the evaporating surface given in Table XII by the figure 1·5 given above, there is obtained the gallons of distillate per hour.

With intermittent distillation, the distillation is often stopped when there is still a small residue which can be run or pumped to other stills for completion. When the distillation is carried so far that "coke" is formed, the effect on the still bottoms is very severe, and in some cases the residue is removed before this stage and the coking effected in special cast-iron stills.

When there is any likelihood of entrainment of oil particles or spray, an oil arrester very similar to a separator used in steam lines is fitted to the vapour pipe from the still. As the vapour velocity is reduced in this arrester, the spray settles out and is returned to the still. This improves the colour and may avoid subsequent redistillation.

Continuous Stills.—When the quantity of oil to be distilled is sufficiently great, continuous methods show to considerable advantage and have become common practice in the larger refineries. A typical installation consists of four stills (600 barrel capacity = 80 tons), each set 6 inches below the preceding one so that the oil flows from one to the other by gravity. The crude oil passes through a cylindrical tank of 300 (American) barrels capacity, where some water separates out owing to the reduced velocity. The oil is then pumped through a heat interchanger, where it is warmed up to 260° F. by the hot outgoing residuum from the last still. The preheated oil enters the first still and is partly distilled therein. It flows from still to still, yielding distillates in each and increasing in temperature. In the last still live steam is added. Table XIII shows the operating data for four stills running on a California oil of 0·897 sp. gr. The daily capacity was 6,696 American barrels when the temperature from the last still was 400 to 450° F., approximately 25 per cent. of the oil being distilled off under these conditions.

TABLE XIII

*Operating Data of Continuous Still Plant at Avon, Cal.**

Temp. ingoing crude .	265	250	260	250	250
Sp. gr. ,, ,, .	0·8945	0·8935	0·9000	0·8935	0·9000
STILL 1.					
Temp. of vapours .	290	290	287	285	290
Sp. gr. distillate .	0·7435	—	0·7435	0·7427	0·7435
STILL 2.					
Temp. of vapours .	340	340	340	340	340
Sp. gr. distillate .	0·7667	0·7507	0·767	0·765	0·7675
STILL 3.					
Temp. of vapours .	386	390	390	387	390
Sp. gr. distillate .	0·7887	0·7896	0·7910	0·7887	0·7878
STILL 4.					
Temp. of vapours .	415	415	415	415	415
Sp. gr. distillate .	0·8090	0·8060	0·8070	0·8055	0·80651
RESIDUE.					
Sp. gravity . .	0·931	0·931	0·933	0·931	0·933

* U.S. Bur. Min. Bull. No. 162, 7.

The volume of oil consumed was 1·1 per cent. of the volume of crude oil distilled. The distillates from these four topping stills were re-distilled in four steam and fire stills and in two steam stills. The water used for condensing averaged about 14 barrels for each barrel of distillate. The heat interchangers consisted of four rows each of five 9-inch casings, 48 feet long, laid parallel and connected by special castings to form a continuous casing. Within the 9-inch casing were five sets of 2-inch continuous pipe coils.

The continuous system gives increased throughput for a plant of a given size, lower fuel consumption and less wear and tear than the intermittent. The initial investment for a given capacity is consequently less. A larger number of fractions, lower fuel consumption and increased throughput are attained in many modern stills as follows. The crude oil is warmed up by the residue from the last still and, if the temperature of this residue is high enough, some of the lighter oils may be distilled off from the crude. The heated oil can then pass in succession through the condensers of the main stills, starting at the first. The oil finally enters the first still and thence flows through the others as before. This arrangement is shown diagrammatically in Fig. 34.

Spray arresters are often fitted where any entrainment is likely to occur, a danger which often arises with heavy crudes containing water in emulsion which causes foaming. Reference has already been made to these traps. Fractional condensers may be and often are added so that the vapour from any still may be subdivided into two or three fractions, which are separately cooled and collected. Although these additions cause complications, yet if a crude of reasonably constant composition is being continuously distilled, much redistillation may be avoided in this way.

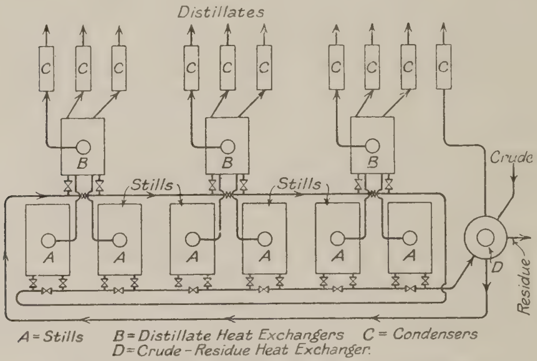

Distillates
C
B
Stills
Stills
Crude
D
Residue
A
A = Stills
B = Distillate Heat Exchangers
C = Condensers
D = Crude - Residue Heat Exchanger.

FIG. 34.—Continuous Stills and Preheaters.

Continuous Pipe Stills.—The tube or pipe still was introduced within comparatively recent years, one of the earliest being installed in the year 1908. This type was originally designed for dehydrating heavy crude oils containing emulsions or for topping, *i.e.*, removal of a small amount of the lighter oils to raise the flash point of the residue until it becomes suitable for use as a fuel oil. Pipe stills have been favourably received by the refiner, are largely displacing the continuous stills described above and are now developed for a great variety of work. The advantages obtained are (1) lower capital cost for a given throughput, (2) simplicity of working, (3) lower fuel consumption.

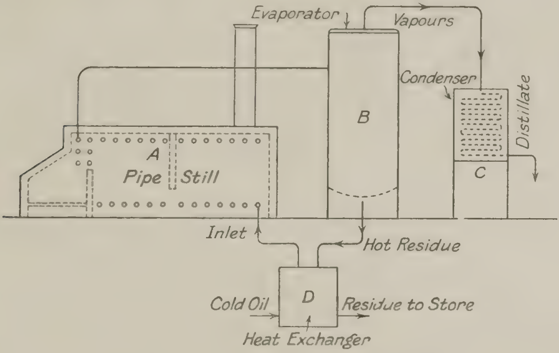


FIG. 35.—Diagram of Pipe Still.

In its simplest form the pipe still, Fig. 35, consists essentially of (A) a furnace with a coil of pipe through which the oil is passed and heated, (B) a steel evaporator or closed tank into which the hot oil is discharged and where the lighter oils are flashed off from the less volatile portion, (C) a condenser to liquefy the light oils thus flashed off, and (D) a heat interchanger where the crude oil is preheated by the outgoing residue from the evaporator. Such a simple still can handle oils containing 15 to 20 per cent. of water and is excellent for removing the light fractions from a heavy crude, but as the vapours leaving the evaporator are composed of several of the fractions obtained from an ordinary straight distillation, it is clear that further separation is necessary. This disadvantage can be overcome to a great extent by fractional condensation, and this is effectively employed in modern plants, of which one of the best known is that of Trumble. As this is typical of these pipe stills as developed and improved, it will be immediately discussed.

Trumble System of Distillation.—In the Trumble system an effort is made to get clean-cut separation of the distillate into the desired fractions by utilising the heat in the vapours, the residue and the flue gases. The distillate is fractionally condensed and the fractions obtained are redistilled in continuous stills incorporated in the plant and having the hot residue from the evaporator as a heating medium. It is convenient to discuss the Trumble plant by referring to an actual installation of the Shell Company at Martinez, California, which does not embody all the latest refinements but is sufficiently typical to serve the purpose. In this connection Fig. 36 shows diagrammatically as far as is possible the flow of liquid and vapour. It has been necessary to omit some of the pipe lines, etc., in order to avoid a complicated diagram, but reference is made in the context to these omissions.

Although not shown in the figure, the crude oil to be distilled is pumped to the plant in a 6-inch pipe and passes through the coolers 1 to 6 in parallel. These coolers are of the tubular type, 30 inches in diameter and containing 62 2-inch by 18 feet tubes. The oil enters the bottom and flows through the tubes in four passes. These coolers are used in connection with the liquid which is fractionally condensed from the vapours passing through the dephlegmators 1 to 6. The oil gains some heat in this way and its temperature is still further raised by heat interchange in the four exchangers

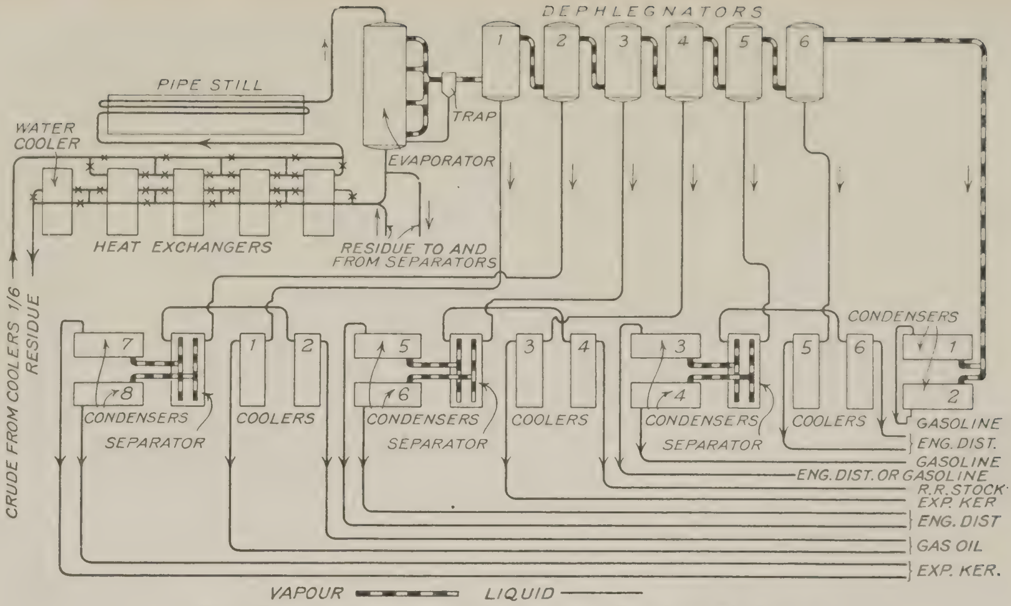


FIG. 36.—Diagram of Trumble Plant at Martinez, California.

through which the outgoing hot residue from the evaporator passes counter-current. Each of these heat exchangers is 4 feet in diameter and contains 178 2-inch by 18 foot tubes. The oil enters each exchanger at the bottom, makes six passes, exits at the top and enters the next exchanger.

From the heat exchangers the oil stream is divided into two parts. Each half passes through 72 4-inch pipes, 18 feet 9 inches long, that are connected into one continuous heating coil by means of return bends. The oil flows through these coils, entering at the lowest point and rising upwards. When it is discharged into the evaporator the temperature is in the neighbourhood of 450° F. (In this plant a " column-evaporator " is used as well as the usual evaporator but is not shown in the figure. See p. 164, Fig. 37.) In the evaporator the oil is converted into vapour and residue.

The residue is used as a source of heat in the three separators (shown in the figure) where the liquids from the dephlegmators 2, 4 and 6 are redistilled before passing to their respective coolers 2, 4 and 6. After leaving these " re-running " stills or separators, the residue passes to the heat exchangers, entering at the top, making two passes around the tubes and leaving at the bottom. In this way it passes through all four heat exchangers in series, but finally passes into a 4-foot tubular water cooler, and then to storage.

The vapours from the evaporator are passed through an oil trap, the entrained oil being returned to the bottom of the evaporator. The vapour passes through six dephlegmators in series, entering each at the bottom and leaving at the top. Fractional condensation occurs in each dephlegmator, forming a liquid that may be a finished product as far as its distillation range is concerned or that may be a mixture that must be separated into two products. These " dephlegmator bottoms," as the liquids are called, are run through the tubular coolers if they are finished products or through the separators if they need to be re-run. The vapours from these separators are condensed in tubular heaters. Thus in Fig. 36 it is seen that the liquid from dephlegmator 1 passes direct to the cooler 1, through which the cold crude is passing as previously described. The liquid from dephlegmator 2, however, passes through the separator 2, where it is partly distilled, the heat being supplied by the hot residue from the evaporator as described. The lighter oils are vaporised and pass to the condensers 7 and 8 as shown.

The two Trumble plants of the Shell Company, during the first eight months of their operations together, ran an average of 16,000 American barrels of crude oil in 24 hours, and vaporised and fractionated 30 per cent. of the crude. The fuel consumption was 1·1 per cent. of the crude oil run and the distillation loss was 0·75 per cent.

The plant is considerably more complicated than would perhaps appear from an examination of Fig. 36, which is drawn to represent the connections when running at one particular time only. There are, however, other pipes and plant which are omitted for obvious reasons. For instance, a number of header pipes are provided so that the liquid from any of the dephlegmators can go to any cooler, and so on. Again small dephlegmators are provided to the separators 1, 2 and 3, as it was found that the vapours issuing therefrom contained too wide a range of hydrocarbons. The diagram is, however, sufficient to give the general outline of the plant.

The Trumble Evaporator.—The Trumble evaporator and column evaporator are shown in Fig. 37. The former consists of a steel shell 6 feet in diameter and 25 feet high. The hot oil from the pipe furnace enters through a 6-inch pipe and strikes the upper spreader-cone, to the serrated edge of which it flows and is distributed so that at least a part of it flows down the evaporator walls in a thin film. The diameter of each speader-cone is about 2 inches less than the inside diameter of the shell. The evaporator is supported in a brick stack whose inside diameter is about 1 foot greater than the outside diameter of the evaporator.

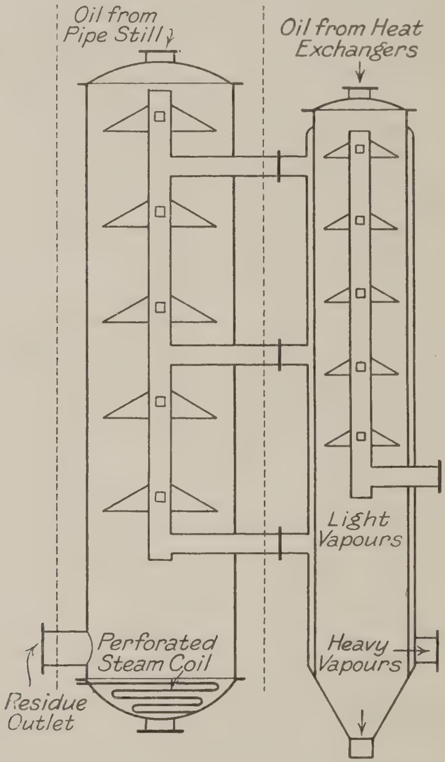


Fig. 37.—Trumble Evaporator and Column Evaporator.

The flue gases from the pipe furnace pass upwards through the annular space and thence to the chimney.

The oil enters the evaporator at a temperature of about 450° F. and with the release of pressure flashes to form a vapour and a residue. The vapour enters the centre pipe through the square opening shown. The residue is heated somewhat as it flows down the side walls owing to the flue gases on the outside. It collects at the bottom and flows away through the outlet shown. A little steam is blown through the hot oil.

The vapour from the evaporator enters the annular space between the cylindrical steel walls of the evaporator column, where it is used to heat the oil flowing down the inner wall of the inside shell. The principle of this apparatus is the same as the evaporator, a vapour and a residue being formed from the oil which has previously been preheated by heat interchange with the hot residue from the evaporator as has been described. The object of the apparatus is to distil off some of the lighter oils after the crude has left the heat exchangers and before it passes to the pipe still. This considerably reduces the pressure in the pipes of the pipe still.

The Trumble Separator.—The Trumble separator consists of a rectangular steel box 6 feet wide by 18 feet long by 40 inches deep. The hot liquid flowing through is partly distilled by the hot residue from the evaporator as already discussed. Small dephlegmators are used in the vapour pipe, 2 feet 6 inches by 7 feet shells provided with a series of internal baffles.

The Trumble Dephlegmator.—The Trumble dephlegmator is shown in Fig. 38. The general construction and principle of operation are easily appreciated. It is 16 feet high and 6 feet in diameter.

Steam Distillation.—Live steam is used in refinery work for re-running gasoline, for reducing burning oil to the desired flash point by removing the lighter constituents and also for bringing lubricating stocks down to the required viscosity. As has been already noted, the crude oil stills are usually provided with open steam coils, but the present discussion applies more particularly to the use of steam in operations subsequent to the primary distillation. In every case the use of live steam enables the oil to be distilled at substantially lower temperatures than would otherwise be possible, so that decomposition is prevented. The reduced temperature is, of course, due to the fact that boiling occurs when the sum of the partial pressures of the oil and steam equals the external pressure. In the case of the lighter distillates the use of live steam has a sweetening effect in that it assists in the removal of bad-odoured or corrosive substances if these are present.

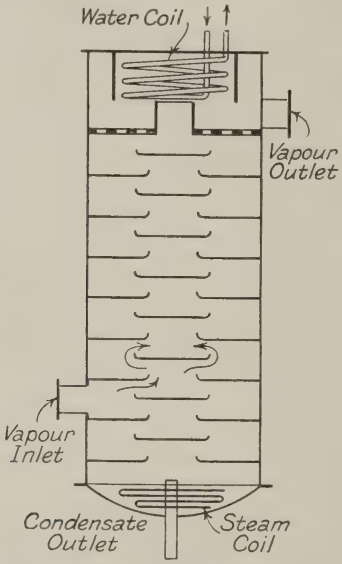


Fig. 38.—Trumble Dephlegmator.

If the light distillate to be re-run does not contain any objectionable constituents the use of steam for heating, evaporating and supplying the partial pressure effect is extravagant, since the generation of the steam requires several times the amount of fuel that is needed to heat the oil by direct fire and to distil at ordinary temperatures. The thermal decomposition of volatile hydrocarbons as the result of distillation without steam is very small and often negligible. The same work can be done by combination fire and steam stills in which the greater part of the heat is supplied by the fire, the live steam being employed chiefly to give the partial pressure effect. All-steam stills provided with both open and closed coils or with closed coils only are also employed.

According to the nature of the operation and the quantities of oil to be handled per day, the distillation may be carried out either continuously or intermittently. A typical continuous still is shown in Fig 39 and includes a scrubbing tower and heat exchanger. The still is divided into compartments by cross-baffles over which the oil flows, the live steam being introduced by perforated pipes at the bottom of each compartment. In the case shown steam heating in closed coils is also provided.

The fractionating columns employed are frequently mere shells filled with broken stone or tile intended to break up the stream of liquid and vapour and to provide fair intimacy of contact. Plate columns with bubbler hoods, Raschig ring columns and similar types of towers are also used. It must be remembered, however, that petroleum products are not required to conform to such close and rigid specifications as are demanded in the case of many coal-tar products such as benzene and toluene. It would not be practicable to isolate the pure hydrocarbons because the oil is composed of such complex mixtures of these constituents. The fractions are collected over certain boiling-point ranges, and even for the smallest range the fractionation does not present any great difficulty. Thus the spirits used for extraction and cleansing purposes which have boiling-point ranges of 90° to 110°, 100° to 120° C. are easily fractionated and hardly to be compared with the problem of separating strong alcohol from its impurities. Motor spirits which have a large distillation range require little fractionation except in so far as it is necessary to obtain a sharp cut between the benzene and kerosene fractions.

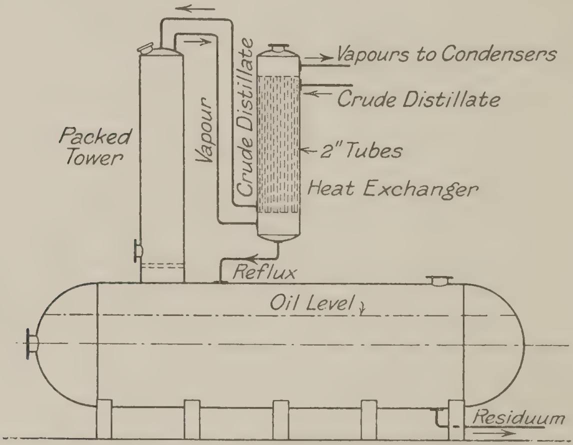


FIG. 39.—Steam Still and Tower.

Distillation Data.—The presentation of any data in connection with petroleum distillation is a matter of considerable difficulty and uncertainty. The information concerning the physical constants is very limited and as a result the design of apparatus is usually based on empirical figures. The exact composition of any particular distillate or fraction is not known, since these are collected between certain temperature ranges or certain specific gravities and not as the pure components of the liquid charged into the still. Consequently only the average specific and latent heats of a given fraction can be considered.

The simplest case to consider is that of a still in which fire heating only is employed, no live steam being admitted. In such a case the accompanying table is presented, compiled from data given by Bell as of practical utility. A paraffin base oil is considered. The specific heat has been taken as 0·5, which is correct for all practical purposes for crude and fractions.

TABLE XIV

Fire Distillation, Paraffin Base Oil

Fraction.	Average latent heat B.Th.U. per lb.	Average temp. vaps. leaving still. ° F.	Average temp. of oil leaving condenser. ° F.	Heat to remove B.Th.U. per lb.	Heat to remove B.Th.U. per gal.
Gasoline . .	130	280	80	230	1420
Naphtha . .	125	325	80	248	1605
Kerosene . .	120	450	100	295	2100
Gas oil . . .	115	540	120	325	2385
Wax dist. or fuel oil	110	650 .	150	360	2590

When live steam is employed in addition to fire the amount used per gallon of distillate varies considerably according to the nature of the crude, the fraction being distilled and the ideas of the process worker. Gasoline and naphtha may be distilled off without steam, but most refiners allow a little to enter from the start. As the distillation proceeds the amount of steam is increased gradually until finally it reaches a maximum during the collection of the wax or fuel oil distillate. In this case the following table is presented, also based on data from Bell, and in it the assumption is made that the quantities of steam used represent maxima and that all the steam introduced into the still has to be condensed. It may be that in any particular case less steam is used and that part of this steam is "trapped" in, say, an air-cooled condenser before entering the condenser proper.

TABLE XV

Fire and Steam Distillation

		Average temp. °F.		B.Th.U. to be removed from				
	Steam lb. per gallon dist.	Vap. leaving still.	Dist. leaving condenser.	Oil per lb.	Oil per gal.	Steam per lb.	Steam per gal. dist.	Total dist. per gal. oil.
Gasoline .	1	250	80	215	1330	1120	1,120	2,450
Naphtha .	1	295	80	233	1510	1141	1,141	2,651
Kerosene .	5	415	100	278	1890	1177	5,885	7,775
Wax dist. or fuel oil .	24	590	150	330	2360	1209	29,016	31,376

In the above table it is clear that the steam at atmospheric pressure is superheated, especially during the latter end of the run. This has been recognised in the calculations.

Condensation Data.—Condenser design is largely based on empirical figures for similar reasons to those given in connection with distillation data. The box and tubular type which were discussed in Chapter VIII are extensively employed. The surface condenser already discussed finds useful service especially in hot, dry climates, while the jet condenser is sometimes favoured, the application of the latter being due to the non-miscibility of oil and water.

The simplest form is that in which there is one long continuous coil submerged in the water contained in a tank, but in some cases the vapours enter a header which connects to a number of shorter coils in parallel, a similar header collecting the condensate from the individual coils. The continuous submerged condenser coil commonly employed consists of several lengths of 10 inch or 12 inch steel, or cast-iron pipe followed by lengths of 8 inch, 6 inch and 4 inch pipe, each length 30 to 40 feet long and all connected into one continuous coil several hundred feet long by means of return bends. Cast-iron pipe, although heavy and awkward, is used when sea-water is the cooling medium or when corrosion of the pipe by acid gases evolved from the crude is probable.

The design is based on empirical data, thus 1·5 to 2 square feet of condensing surface per gallon of gasoline or naphtha per hour, of 1·2 square foot for kerosene and 1·0 square foot for heavy oils is usual, but these figures must be modified to suit the particular conditions. This data is equivalent to designing on the basis of $H = 13{\cdot}5$ to $18{\cdot}5$ B.Th.U. per hour per square foot per 1° F.

In the case of parallel coils of relatively small diameter the rate of heat transmission may be 20 to 25 per cent. more favourable under otherwise equal conditions. Both the continuous and parallel pipe coils have been modified to give a larger amount of surface per foot run by using radiator sections provided with ribs or flanges at right angles, and the condensing capacity can be increased 20 per cent. over a pipe of comparable dimensions. These cast-iron sections can be made so compact that a condenser tank only half the size of that needed for an ordinary continuous coil is necessary for the same condensing surface.

Open surface condensers occupy very much less space than the box type and are made up either of straight lengths of tube or cast-iron radiator sections, in all cases the cooling water running parallel with the vapour to be condensed.

Tubular condensers if suitably designed can give a high rate of heat transfer. Values of the coefficient of heat transmission may vary from 8 to 30 B.Th.U. per hour per square foot per 1° F.

The following small table gives the values of H as recommended by Bell for different services.

TABLE XVI

Coefficient of Heat Transfer. Condensers

	Submerged continuous coil.	Submerged parallel coil.	Tubular.
Oil vapours .	6	7·5	35
Steam . .	50	62·5	250

CHAPTER XI

COAL TAR

Coal tar is the thick black viscous liquor obtained as a by-product from the carbonisation of coal in the manufacture of coal gas. It is a very complex mixture of many substances but its exact composition is practically unknown. On distillation a number of substances are obtained which are of great value for many different purposes.

The composition of tar varies enormously according to the mode of its formation and depends on the kind of raw coal used, the temperature of carbonisation, the kind and shape of retort, the depth of the coal in the retort and many other factors which need not be enumerated here. In addition to coal tar the distiller may have to deal with coke oven tar and blast furnace tar. Coke oven tar usually contains less naphthas and phenols than gas tar, but can be mixed and distilled with it. Blast furnace tar is very different and must be distilled separately.

Dehydration of Tar.—The tar as received is generally allowed to settle in large underground wells or tanks, the tar sinking to the bottom, leaving the water on top. In this way it is possible to bring the water down to about 5 per cent., although in some cases where an emulsion has been formed partial dehydration is not possible. This water is ammoniacal liquor, but the subsequent treatment of this will not be considered here.

The usual method used for removing the water is to warm the tar in a fire-heated still until the temperature reaches about 212° F., when the water commences to boil. Firing is then discontinued, and on allowing the liquid to settle for a short time it is found that nearly all the water is separated as a layer on top of the tar. This water layer can be run off by a suitable tap or other simple means.

Ordinary Tar Stills.—Some reference has already been made in Chapter VII to these tar stills, and it is only necessary to refer to Fig. 40, which shows a still with concave bottom and a swan neck outlet for the vapours. These vapours pass through a coil in a preheater on the same principle as in the case of the simple brandy still illustrated in Fig. 25 of Chapter IX. If the preheater coil is designed with sufficient heating surface, enough heat can be extracted from the vapours passing through to distil off all the water and some of the lighter constituents in the raw tar. In this way when the distillation in the still is completed and the pitch has been run off the charge in the preheater can be run hot into the still.

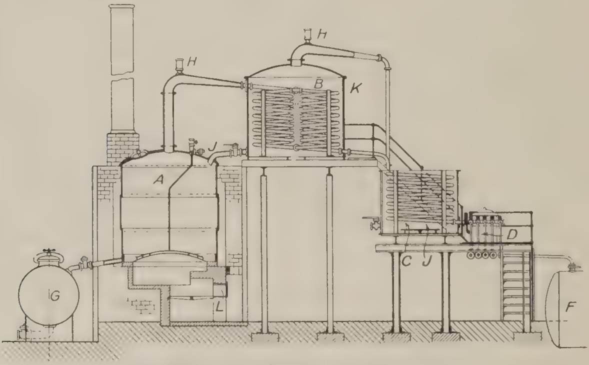


FIG. 40.—Tar Still and Preheater.

The vapours from the still and the preheater are condensed in separate coils and the condensates run to suitable receivers. The coil in the preheater is usually made of wrought iron, but the final condensers are of cast iron, a metal which, although it makes a heavy and cumbersome coil, is most suitable for resisting corrosion. Lead coils are sometimes used, but their high initial cost detracts from the advantages that they offer.

Fractions.—The number and the kind of fractions taken off when tar is distilled depend on the quality of the crude and the market value of the various products obtained therefrom. If the extraction of any particular product is not warranted owing to market conditions it may be necessary to effect some changes. Roughly speaking, however, the fractions taken off are as follows :—

First Fraction.—This will consist of water (ammoniacal liquor) and naphtha, which is a mixture of benzene, toluene, xylenes and pyridine. The naphtha floats above the watery layer, with which it is not miscible, and which is drawn off from the bottom and sent to the ammonia works. For a given tar the amount of ammoniacal liquor in the first fraction will depend on whether previous dehydration has been carried out or not.

The boiling-point range of the first fraction is approximately from 180° to 280° F.

Second or Light Oil Fraction.—This fraction contains the higher hydrocarbons of the benzene series, the higher homologues of pyridine, some phenol and some naphthalene.

The boiling-point range of this fraction is approximately from 280° to 390° F.

Third or Middle Oil Fraction.—This fraction contains phenol, the cresols, considerable naphthalene and creosote. The danger of naphthalene crystallising in and blocking the condenser tubes renders it necessary to maintain the condenser water at a high temperature either by shutting off the water supply before the cut for the third fraction or by admitting live steam into the condenser tank. The safety valves shown on the swan-necks in Fig. 40 are provided in case excessive pressure should be developed.

The boiling-point range of this fraction is approximately 390° to 580° F.

Fourth or Creosote Oil Fraction.—This contains naphthalene, much heavy oil, complex hydrocarbons and phenol homologues.

The boiling-point range of this fraction is approximately 580° to 660° F.

Fifth or Anthracene Fraction.—This fraction contains anthracene salts, which are liable to bring about an obstruction in the condenser coil unless the condensing water is kept at a high temperature; at its boiling point is best. After the fraction has been running for a short time firing is slackened and live steam introduced into the still. This steam reduces the tendency of the residual pitch to coke and therefore prolongs the life of the still bottom.

The point at which the distillation is stopped depends upon the quality of the pitch which is desired.

Pitch.—The residue of the still is allowed to remain there to cool for a period before running into the pitch cooler. This minimises the risk of damage to the still and its brickwork, puts less strain upon the cooler and reduces the danger of the pitch taking fire.

Continuous Tar Dehydration.—The word dehydration is very loosely employed in connection with tar distillation, and as often as not is meant to imply that some naphthas and light oils are removed in addition to the ammoniacal liquor, the object in view being the production of a tar suitable for use on roads. In such cases the resultant tar is termed "dehydrated." The Wilton plant for this purpose consists of a cast-iron coil contained in a furnace where it is heated by a fire of coke breeze or small coke. The coal tar is pumped through an economiser coil or heat interchanger, where it is heated by the dehydrated tar leaving the plant. The heated tar then passes to the coil or pipe still, where its temperature is raised to between 280° and 430° F. as required. A small pressure is maintained on the coil by a relief valve, but when the hot tar passes this valve it enters a vapour box at atmospheric pressure, where the water and light products are flashed off as vapour: The dehydrated tar gravitates to the economiser and thence to storage. The vapour condenses in a coil and is collected in a separating box in the form of ammoniacal liquor and light oil.

It is clear that the principle is the same as that of the pipe still used in petroleum distillation and illustrated in Fig. 35. On the average the fuel consumed is 190 lb. of coke breeze per 1000 gallons of tar treated.

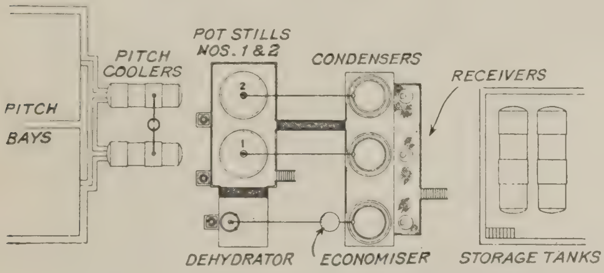


Fig. 41.—Wilton Dehydrator and Pot Stills.

Semi-continuous Tar Distillation.—The Wilton dehydrating still described above can be combined with pot stills as shown in Fig. 41. In this case the dehydrated tar is passed into the one pot still while the other one is working, so that semi-continuous working is possible. The pipe still works continuously and the two tar stills intermittently and alternately. By employing three pot stills one still can be filled while another is being worked off and while the third is cooling down before tapping the pitch.

Continuous Tar Distillation.—The Wilton continuous still is based on the principle of fractional condensation. The tar is heated in an economiser by the pitch leaving the plant and passes thence through the pipe coil still into a vapour box. The vapours are flashed off as before, and pass in succession through two condensers, in the first of which the heaviest portions of the vapour are condensed out while in the second the remaining, and more volatile components are liquefied. The principle of working is similar to that of the Trumble evaporator, and it is said that the number of fractions can be increased by increasing the number of condensing units. The temperature to which the tar is heated in the pipe still and the pressure in the coil will vary according to the particular tar being distilled and to the number of fractions required.

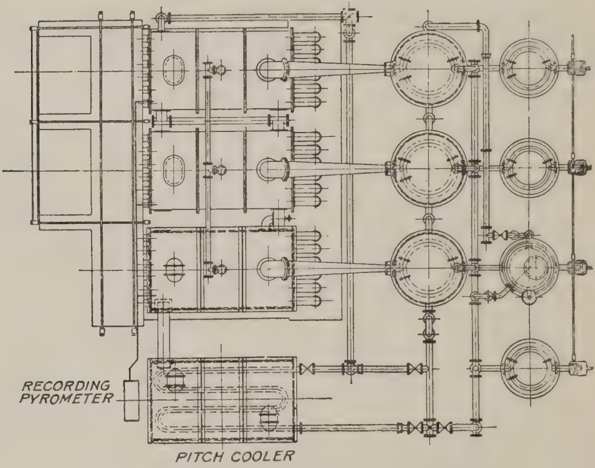


FIG. 42.—Hird Continuous Tar Stills.

The Hird distilling system consists of a series of small stills, each of which is responsible for distilling off one fraction from the tar as it passes through them in succession, the principle being similar to that employed for petroleum (p. 158). Fig. 42 shows the plan of three such stills, this number usually constituting a set, although four are often used. Heating is internal, hot gases being passed through steel tubes immersed in the tar, except in the last still, where live steam is employed to remove the anthracene oil, in the same way as this fraction is removed in the case of a discontinuous pot still. Each still is provided with a heat interchanger and a water-cooled condenser. Each heat exchanger has a vapour take-off to a common main which is connected to the fourth condenser shown in the figure.

The tar passes in succession through each of the heat interchangers, through a coil immersed in the pitch cooler and into the first still. It then passes through the other two stills, the residual pitch flowing from the last still into the pitch cooler. Four fractions are thus obtained, viz., light naphtha from the preheaters, and middle oil, creosote oil and anthracene oil from the three stills.

Treatment of Naphthas and Light Oils.—The first and second fractions obtained from the distillation of crude tar contain the naphthas and light oils from which the various qualities of benzols and naphthas are obtained. Both fractions contain varying amounts of tar acids, pyridine bases and impurities which must be removed, but the degree to which the main constituents are separated depends on the demand. The production of pure benzene and toluene is no longer required in such great amounts as was necessary during the war, and cruder fractions may in many cases be as much as is needed. It is beyond the scope of this book to describe in detail the plant and methods used in the various washings to which the fractions obtained are subjected in the course of their distillation, but a brief reference will be made to the general principle.

Washing of Fractions.—It has been stated above that both the first and second fractions contain tar acids and pyridine as well as impurities. The amount of acids should be small if they have been extracted in the way to be described in connection with the recovery of carbolic and cresylic acids. If this has not been done, or if there is still an appreciable amount of such acids present, they can be extracted by washing with caustic soda, which forms the sodium salt, sodium phenate being obtained in the case of phenol and corresponding salts with the homologues. The tar acids are subsequently separated from the salts by treatment with mineral acids. Pyridine bases, on the other hand, are converted into sulphate by the action of sulphuric acid with subsequent recovery by neutralisation with alkali. The recovery of pyridine bases is often carried out in conjunction with the manufacture of sulphate of ammonia.

Primary Stills.—The primary distillation is effected in either a fire- or a steam-heated still provided with a fractionating column, but only a final condenser, no partial condenser being employed on account of the high temperatures. The object of the distillation is to obtain crude fractions, which are then subjected to greater separation.

If a fire-heated still is employed, the design of such is on the same lines as those of an ordinary tar still except that the capacity is smaller, 2000 to 3000 gallons being common. The column may be of cast iron or steel provided with either perforated plates or bells. A preheater such as has been described in connection with the pot stills can be usefully added, the heat in the vapour from the top of the column being partly used to preheat the next still charge instead of being entirely lost in the condenser water. If a steam-heated still is used the capacity would be about the same as that of the fire-heated type. In both cases open steam is provided from the use of which these stills are often known as "blow-over" stills.

Final Stills.—The crude fractions obtained in the primary distillation are washed and subjected to further distillation. For the fraction called "crude heavy solvent," which will be discussed shortly, a fire-heated still such as is used for the primary distillation would be employed. For the lighter fractions a steam still provided with a column, partial and final condensers is employed, as close fractionation is necessary, assuming that pure benzene and toluene are required. The work is, of course, much simplified if only 90's benzol and 90's toluol are desired.

Continuous Stills.—Numerous attempts have been made to give continuous fractionation of crude naphtha and some successful plants have been evolved. The Adam Continuous Still is a good example of a satisfactory apparatus for this purpose. The principle is very similar to that of the Hird still already described in connection with tar distillation. There are three stills, each of which is responsible for distilling off one fraction and through which the crude flows in succession. The first and second stills are provided with fractionating columns and partial and final condensers, but the third has a fractionating column and final condenser only, the partial or reflux condenser being omitted on account of the high temperatures. The fractions obtained are benzol, toluol and solvent naphtha, which are subsequently re-worked for the pure products.

Distillation of Naphthas and Light Oils.—There are a number of ways in which the distillation and washing of the naphthas and light oils can be effected, but all these cannot be discussed here. A general idea of one suitable method is given in diagrammatical form in Fig. 43.

First Distillation.—The crude naphtha or light oil is distilled in a fire still giving four fractions, crude benzol, crude solvent and crude heavy solvent. The residue in the still contains creosote and naphthalene, and is treated for recovery of the naphthalene.

Second Distillation.—The crude benzol fraction from the first distillation is washed to remove the impurities. If there are phenols present they are extracted with caustic soda, but the pyridine bases are removed with acid as previously outlined.

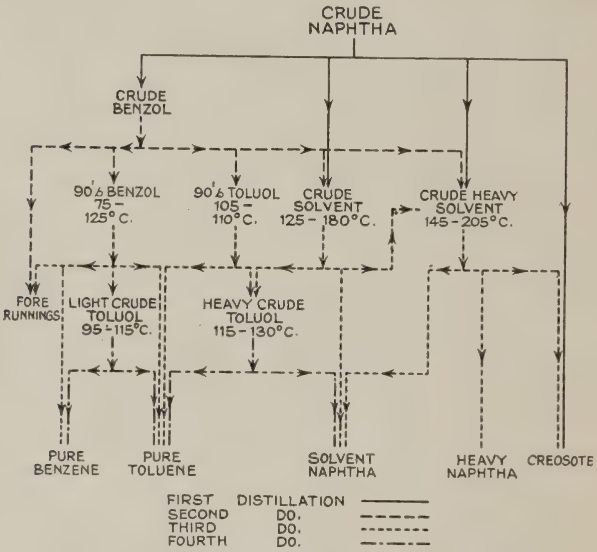


FIG. 43.—Distillation of Naphtha. (Butler.)

The washed crude is then distilled in a steam-heated still with a column and two condensers, the fractions obtained being 90's benzol, 90's toluol, crude solvent and crude heavy solvent. The residue in the still is mostly creosote, but may be put back into the crude naphtha for further working.

Third Distillation.—The 90's benzol is distilled in a steam still as before and gives forerunnings, pure benzene, light crude toluol and pure toluene. To the residue in the still is then added the 90's toluol from the second distillation, the fractions obtained on distilling this mixture being light crude toluol, pure toluene and heavy crude toluol. To the residue left after this distillation is added the crude solvent obtained from the first and second distillations, the former having been washed with acid and alkali to remove the impurities. The fractions obtained are heavy crude toluol, solvent naphtha and crude heavy solvent, the distillation of the second and third being effected with the assistance of live steam.

The distillation of the crude heavy solvent is effected in a fire still with a column but no partial condenser. The charge comprises the fractions from the first distillation in a fire still, the second distillation in a steam still and the third distillation in a steam still just mentioned above. The first of these will have been washed to remove impurities. The fractions obtained from the heavy crude solvent are solvent naphtha and heavy naphtha, the residue in the still being creosote.

Fourth Distillation.—The light crude toluol is distilled in a steam still, giving pure benzene and pure toluene. To the residue in the still is added the heavy crude toluol, and from this new charge there are two fractions, pure toluene and solvent naphtha.

The three xylenes, meta, para and ortho, are usually sold as a mixture, as the pure products are rarely required. Fig. 43 represents approximately the progress of the distillations, smaller intermediate fractions which are actually obtained being omitted.

Recovery of Carbolic and Cresylic.—The naphtha, light oil and carbolic fractions in the distillation of tar contain varying amounts of tar acids such as phenol, the acid content increasing up to the third fraction. These tar acids are extracted by washing with caustic soda, which forms sodium phenate and sodium cresolate, commonly known as carbolate and cresolate. The acids are recovered from these sodium salts by treatment with mineral acid. The fourth or creosote oil fraction, although it consists mainly of creosote oil, contains a certain amount of tar acids, which may be distilled off and similarly extracted.

The washing of the crude oils for the extraction of the tar acids and the crude separation of phenol and the cresols in the form of carbolate and creolate are effected together. This crude separation is based on the fact that if a solution of carbolate containing a little carbolic and much cresylic acid, or perhaps all cresylic acid, is added to an oil rich in carbolic acid, the carbolic acid in the oil displaces the cresylic acid in combination with the soda in the carbolate. The cresylic acid goes into solution in the oil, and the carbolic acid goes into the aqueous solution. This aqueous solution settles to the bottom of the washing vessel on standing for a while and can then be drawn off. Other washes with different strengths of carbolate may be needed, but finally the oil in the washer becomes relatively rich in cresols, most of the phenol having been extracted. The cresols and homologues can now be extracted by washing with a clean solution of caustic soda.

To regain the acids from the solutions thus obtained, the sodium salts may be decomposed by mineral acid, but the usual method is to use carbon dioxide gas, which unites with the sodium to form sodium carbonate. The liberated tar acids float above the sodium carbonate solution and are easily run off. The carbonate is used in the manufacture of caustic soda for subsequent washes.

Refining Tar Acids.—The crude carbolic and cresylic acids are, as the names imply, rich in phenol and cresol respectively. The crude carbolic which contains a certain amount of water can be distilled in a pot still, giving crude fractions of water, phenol and cresol. The phenol in the second fraction is separated out by fractional distillation and fractional crystallisation, but these will not be discussed here.

The cresols in cresylic acid and those obtained in the rectification of the carbolic acid can be treated together. Orthocresol (B.P. 191) can be separated from the meta- and para-cresol by fractional distillation, but the meta cannot be separated in this way from the para, since there is only 1° C between the boiling points. Many attempts have been made to effect this separation, but in only one case has success been obtained on a commercial scale, and for this the author built the necessary plant.

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